THERMODYNAMICS

P. C. RAKSHIT

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(For Honours and Post-Graduate Courses)

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To

THE MEMORY

of

MY BELOVED SON

PREFACE TO THE FOURTH EDITION

In revising the last edition of this book, such drastic modifications and changes have been made that this edition is, in reality, a new book. Besides, a considerable amount of new matter has been added. In doing this, the goals of clarity, depth and accuracy were always kept in mind. The main objective of this text is to make the reader familiar with the basic principles of thermodynamics and the modes of their application and to prepare him for an extended work in this field. Attempts have been made to give careful definitions and explanation of concepts followed by simple mathematical expressions. In spite of the diverse application of thermodynamics, the topics have been so organised in this text that the student can perceive the broad nature of the logic of its laws rather than feel that he is bombarded with a plethora of mathematical formulae. It must be remembered that as an exact science the beauty of thermodynamics lies in its logical structure and the precise deductions from the same. Every effort has been made to preserve it. To make the meaning of the formulations clear, illustrative problems have been worked out in each case. Moreover every chapter is followed by new pertinent exercise problems which would help the student to understand the principles involved thoroughly.

During the past few years the author has received from professors of universities and colleges many letters containing corrections and suggestions for changes in the book. I am indeed very grateful to them and I express my sincere thanks to all of them for this hlep. My thanks also go to my many younger colleagues and students whose constant questionings have helped me a lot.

P. C. RAKSHIT

Calcutta
May, 1983

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THERMODYNAMICS

CHAPTER 1

FUNDAMENTAL CONCEPTS

1.1. Introduction

Thermodynamics, literally speaking, concerns itself with the flow of heat and conversion of heat into work. Heat, as we know now, is a form of energy and the science of thermodynamics now governs not only the transformation of heat into work and *vice versa* but also includes all types of interconversion of one kind of energy into another, e. g., electrical energy into work, chemical energy into electrical energy etc. It is based on three simple but empirically derived laws of nature, acquired from long experience. The laws of thermodynamics can be subjected to rigorous mathematical treatment and they have yielded correlations between different observable properties of macroscopic quantities of matter, such as pressure, temperature specific heats, coefficients of expansion, latent heats, density etc. These relations, thus predicted, have been confirmed by experimental tests for more than a century in different systems from the heat-engines to the enzymatic processes in a living cell. The most distinguishing feature of thermodynamics, however, is its predominant concern with temperature and tempratrue-dependent variables.

Predictions of the physical properties of matter can be made by analysing the behaviour of a large-scale or macroscopic amount of the matter. This can also be done by statistically averaging the behaviour of the individual particles which constitute the matter. Generally, thermodynamics does not take into consideration the existence of individual particles and their characteristics. This is *classical thermodynamics*. The classical thermodynamics does not make any hypothesis as to the structure of matter. In contrast to the kinetic-molecular theory, it derives relations between propreties experimentally observed but does not offer any explanation why these properties arise in a system. The approach in thermodynamics is thus entirely different from that in the atomic constitution of matter. For example, in the kinetic theory we consider the pressure of a gas as a measure of the impact of the molecules on the wall per second, while in thermodynamics, pressure is a property of the state of a system regardless of its inherent constitution, based on the observation of the body as a whole. Likewise, temperature is, according to the kinetic theory, a measure of the average kinetic energy of the molecules while it is a simple property of state from the viewpoint of thermodynamics. To obtain a better insight into the reason of the existence of different properties of matter, it is necessary to incorporate the molecular theory into the thermodynamic postulates with the help of mechanics. This leads to *statistical thermodynamics*, as distinct from the classical thermodynamics.

In its application, the thermodynamics usually relates to macroscopic bodies [containing at least a weighable quantity]. Its formulae would not however conform to the behaviour of systems containing submicroscopic amounts, say, of a few molecules. The pressure of a single molecule or the temperature of a single molecule has little significance here.

The basic principles of classical thermodynamics were established during the second-half of the last century. The most important contributions came form Rumford, Carnot, Mayer, Joule, Clausius, Kelvin, Helmholtz and others.

Thermodynamics is essentially a practical science and it has its ramifications extending mainly to the fields of chemistry, physics and engineering. To illustrate, with the assistance of thermodynamics the chemist predicts the possibility of a chemical reaction or the maximum yield in a chemical process under a given set of circumstances ; using thermodynamic laws the physicist explains the phenomena where phase changes or inter-actions with radiations or electro-magnetic fields are involved; to the engineers it is the most powerful weapon to solve the problems of power and combustion, in the prediction of efficiencies of heat-engines and refrigerators, in the design of engines and so on. In fact, in many branches of science, it is almost an indispensable tool.

Inspite of the fact that the thermodynamic relations are generally valid in countless number of cases we must be carefully conscious of their limitations too. The thermodynamic principles correlate different observable properties of a system but cannot always give us the exact magnitude of a property of the system. These relations help us in predicting the behaviour of a system or the ultimate result that a process would lead to. Thus, from thermodynamics, we can predict under a set of defined conditions the maximum yield in a chemical process, but we cannot say anything about the rate of the reaction or the mechanism of the reaction.

In this text generally the stress will be placed on the macroscopic viewpoint. The relations of classical thermodynamics so obtained are quite satisfactory and helpful in the understanding of various problems. But whenever necessary, the molecular or statistical viewpoint would also be invoked to interpret and explain a phenomenon or property, such as entropy.

1.2. Temperature

The hotness or coldness of an object is comprehended fundamentally by our sense of touch. Commonly we use the word *temperature* to understand the comparative warmth of a body. The hotter body will have a higher temperature than the colder one.

Suppose there are two bodies A and B, A being hotter than B. If A is brought in contact of B it is found that A gradually becomes colder and B gets warmer. During this process, other changes in pressure or volume may also occur. Ultimately both A and B are found to be equally warm, i.e., they have attained the same temprature. A and B are now said to be in *thermal equilibrium*. In this process some energy (namely the heat energy) have moved from the hotter body A to the colder body B. Temperature then determines the direction in which heat would flow, i.e., from the hotter to the colder body. We may conclude, '*temperature is the driving force for the flow of heat*'. When the two bodies are at the same temperature, no heat would pass from one to the other. Maxwell thus stated: "*the temperature of a body is its thermal state considered with reference to its ability of communicating heat to other bodies.*"

Suppose we have three bodies X, Y and Z such that X is hotter than Y and Y hotter than Z as revealed by sense of touch. Then, X is also hotter than Z. This is similar to numbers. If p, q and r be three numbers such that if p is larger than q and q larger than r, then p shall be larger than r. It is thus obvious that if we could assign some values to hotness so that the hotter body will have a higher value, then those values might be regarded as temperatures of the bodies. The basis of fixing the value in relation to relative degrees of hotness will have to be abitrary.

Consider now three systems A, B and C. Suppose A is in thermal contact with B through a *diathermic wall* and again B is also similarly in thermal contact with C (Fig. 1a). A 'diathermic wall' is that which permits the systems in contact to influence each other, so that their coordinates (p, v etc.) may alter and such a wall permits the flow of heat through it. Sufficient time being allowed, A will be in thermal equilibrium with B ; C also will be in thermal equilibrium with B. If B is now removed and A is brought in thermal contact with C, it is found that there is no change in the coordinates of A and C. That is the systems A and C are in thermal equilibrium with each other. Hence it is stated :

"*Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.*"

This is often mentioned as the '*Zeroth law of thermodynamics*'. In fact, all measurements of temperature are based on the truth of this statement.

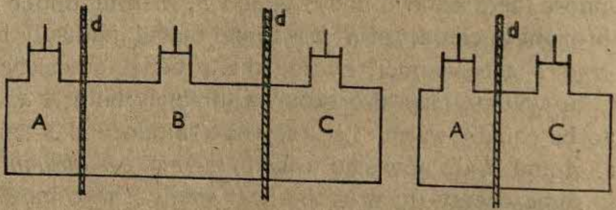

Fig. 1a

Now, systems which are in thermal equilibrium have the same hotness experienced by our senses. Or, we may say, systems in thermal equilibrium with each other must have the same temperature. So long the systems are not in thermal equilibrium, they will have different temperatures. Temperature thus becomes a property of a system which determines if it would be in thermal equilibrium with other systems.

We may proceed to examine this a little more thoroughly. Suppose there are two separate systems X and Y, each in its own equilibrium state. For convenience of understanding, let the systems be gaseous ones. The states of their existence are defined by two variables, pressure and volume, which will determine the different properties of the systems including hotness. Let p, v be the pressure and volume of the system X, and P and V those of system Y. Now suppose the two systems are brought in contact through a diathermic wall. The pressure and volume of the two systems would change. Let p_1, v_1 and P_1, V_1 be the new magnitudes of those variables when thermal equilibrium is attained. If the system X be now separated, it is an observed and established fact that its variables p_1, v_1 may be altered to a new set (p_2, v_2) or to a set(p_3, v_3)etc. and yet X remains in thermal equilibrium with Y, having pressure and volume, P_1, V_1. It means that X may have many states represented by (p_1, v_1),(p_2, v_2), (p_3, v_3), . . . all of which would be in equilibrium with (P_1, V_1) state of system Y, and (from *zeroth law*) are in equilibrium with each other. If now these p-v values of system X be plotted graphically, we come across a curve (Curve A) which may be called an *isotherm* since all these states are in thermal equilibrium (see fig. 1*b*). This isotherm is the locus of all points representing states of X-system in thermal equilibrium with (P_1, V_1)-state of system-Y.

Similarly with system-Y, we shall have a set of states given by (P_2, V_2), (P_3, V_3) . . . all of which would be in equilibrium with state (p_1, v_1) of system-X, and hence are in equilibrium with one another. These sets of P-V values may be plotted for system-Y to obtain a corresponding isotherm curve B.

All states of system-X represented by isotherm A will be in thermal equilibrium with any state of system Y, represented in corresponding isotherm curve B. It may then be said that these systems in the given states have a property by virtue of which they remain in thermal equilibrium with one another. This property is the *temperature*. It is thus a property of the system and, as mentioned earlier, it determines whether the system would remain in equilibrium with other systems. This idea is also consistent with our experience that when two bodies are in contact for long, they acquire the same degree of hotness to our touch.

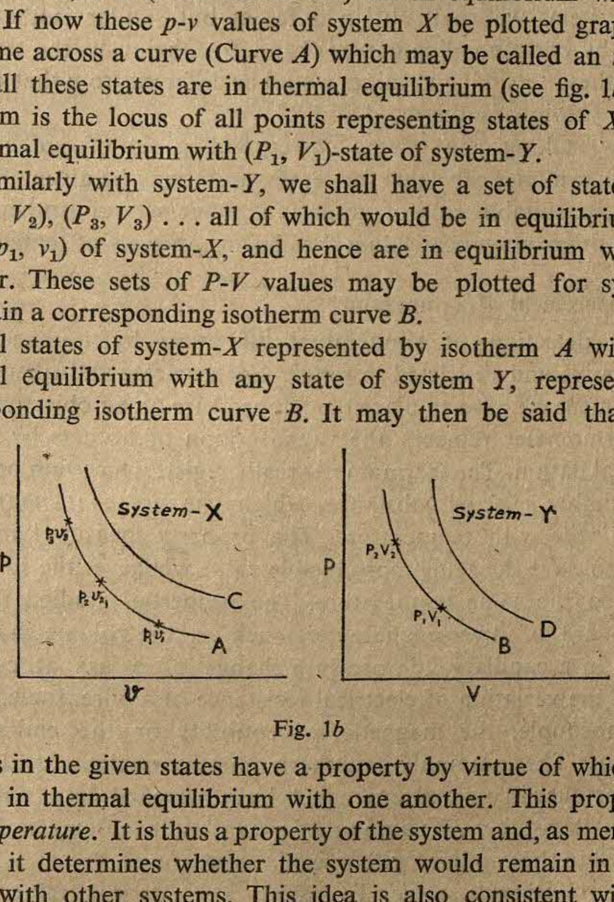

Fig. 1*b*

Mathematically, we can express the equation for p-v isotherm curve A in the form; $\phi\,(p,v) = t$ (constant),
and for curve B, $\psi\,(P,V) = t'$ (constant)

If we insert a suitable number in one of these functions, it is easily possible to make $t = t'$, so that we have

$$\phi(p, v) = \psi(P, V) = t$$

This function (t) is thus a property based on (p,v)-values of all states of curve A and is the same for all other states in curve B and is the temperature.

Again, starting with different initial sets of (p-v) values for X- and Y-systems we shall obtain different but similar isotherms as denoted by corresponding curves C and D. Obviously, the temperature for these sets of (p-v) values would be different from that obtained in the previous isotherms A and B.

Now, taking one of the corresponding set of isotherms as reference, a numerical value for temperature may be given. Further adopting a suitable rule of gradation, other sets of isotherm will be given other numerical values thus framing a scale of temperature.

1.3 Measurement of Temperature

The detection of temperature-differences by human senses is qualitative and restricted in range. For accurate and quantitative measurement we have to place the temperature on an objective scale. The thermometer replaces the vague notion of hotness by precise numerical datum. The thermometer really registers a certain property (of a suitably selected substance) which changes *continuously and monotonically* with temperature. The property measured must be such as to have the same reproducible value whenever the substance returns to the same temperature. The properties studied for this purpose are of diverse character, such as the volume-change of a liquid in a capillary, the pressure-change of a gas at constant volume, the variation of electrical resistance of a wire, the e.m.f. of a thermocouple, the magnetic susceptibility or the emission of radiations. The commonly used thermometer contains a small quantity of mercury in a small evacuated bulb attached to a uniformly capillary glass-tube. The amount of expansion in volume is linearly measured in the capillary with rise of temperature.

The Centigrade Scale. To assign a numerical value to the level of hotness, we have first to fix a standard datum line (*i.e.*, zero point) and a unit for expressing the magnitude. For this purpose two fixed points, the ice-point and the steam-point, are universally selected. These are the freezing and the boiling temperatures of water under one atmosphere. These are the standard references. Let us now say that the magnitudes of the property P (whose variation would signify the temperature) have values P_i and P_s at the ice-point and the steam-point respectively. Further let this difference of the P-values between two fixed points be divided into 100 equal divisions, each division corresponding to one degree of temperature. This property P may be the expansion in volume of a liquid or the resistance of a wire or the pressure of a gas, etc.

The unit of temperature would then be $1° = \frac{P_s-P_i}{100}$ and this is the unit in the centigrade scale (°C). Then a body having a temperature t°C will have the property P such that

$$t°\text{C} = \frac{P_t-P_i}{(P_s-P_i)/100} = 100\frac{P_t-P_i}{P_s-P_i}$$

If we further designate the ice-point where $P=P_i$ as 0°C, the point $P = P_s$ would be 100°C. In the mercury thermometer, the expansion of volume of mercury is measured in the uniform capillary and hence the expansion is proportional to the length of mercury column in the capillary from the ice-point. Then

$$t°\text{C} = 100\,\frac{l_t-l_0}{l_{100}-l_0}$$

The difference in the P-values between the ice-point and the steam-point may be subdivided into any desirable sections instead of 100 divisions. This will only alter the units (*i.e.*, degrees) of temperature. Likewise, the standard datum line at the ice-point may be given any arbitrarily chosen value instead of zero. So, in Fahrenheit scale, ice-point is 32°F and the range between ice and steam points are divided into 180 Fahrenheit degrees. Hence one centigrade degree is equal to 9/5 degree farhenheit. So, we have,

$$t°\text{C} = \left(\frac{9}{5}t + 32\right)°\text{F}.$$

The Absolute Scale. Thre is yet another scale of temperature called the 'absolute scale' which would be referred more frequently in our subsequent discussions. This scale has been drawn up on the variation of the pressure of a gas (at constant-volume) with temperature. It is well known that the pressure of a given mass of gas at constant vomume increases continuously with rise in temperature. But under ordinary circumstances, the increase in pressure of different gases [at const. vol. with a given quantity] with equal rise in temperature is somewhat different.

Then suppose in this scale of temperature, the temperature at the ice-point be θ_i when pressure is P_i and let the temperature be θ_s when pressure is P_s, the volume and mass of the gas taken remaining unaltered. Let the difference of pressures between the two fixed points be divided into 100 equal parts (as in the centigrade scale). Then one absolute degree $\equiv \frac{P_s - P_i}{100}$ and further let $\theta_s - \theta_i = 100°$ absolute, such that one absolute degree ≡ one centigrade degree.

Now, for a given mass of gas kept at any desired constant volume V_i, we can experimentally determine both P_s and P_i, It has been found that at low pressures $\left(\frac{P_s}{P_i}\right)_v$ bears a linear relationship to P_i. The values of P_i may be altered by changing the volume to different constant magnitudes in different experiments. The straight lines obtained by the plot of $\left(\frac{P_s}{P_i}\right)_v$ against P_i for different gases would be somewhat different (Fig. 1c). If these lines be extrapolated to $P_i = 0$, then in all cases, the straight lines cut the $\left(\frac{P_s}{P_i}\right)_v$ -axis at the same point, such that

$$\underset{Lt\ P_i \to 0}{\left(\frac{P_s}{P_i}\right)_v} = 1.36609$$

It must be understood that it is not presumed that pressure of the gas vanishes but that P_i, the pressure at the ice-point is made infinitely small. Though the magnitude of $\left(\frac{P_s}{P_i}\right)_v$ is obtained from the properties of real gases, the ultimate limiting value of the same is independent of the nature of the gas.

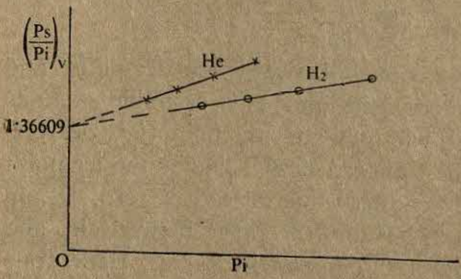

Fig. 1c

In defining the absolute scale we further designate that

$$\frac{\theta_s}{\theta_i} = \underset{Lt\ P_i \to 0}{\left(\frac{P_s}{P_i}\right)_v} = 1.36609$$

It means that the temperature would be directly proportional to the pressure (at constant volume) a condition held valid for ideal gases only. Now, we have two relations:

$$\frac{\theta_s}{\theta_i} = 1.36609\ ; \qquad \theta_s - \theta_i = 100°$$

whence $\theta_i = 273.15°$ Abs.; $\theta_s = 373.15°$ Abs.

In this absolute scale, therefore ice-point would be 273.15° Abs. and since the degrees in the scale are identical with centigrade degrees, the zero-datum of this scale would be 273.15° below the ice-point. Further, any temperature $\theta°$ Abs. of a body would be $\theta = (t°\text{C} + 273.15°)$ Abs.

Absolute temperatures measured in Fahrenheit degrees are called Rankine degrees, sometimes used by engineers.

One absolute degree ≡ 9/5Fahrenheit degree.

∴ 273.15° absolute degrees ≡ 491.6° Fahrenheit degrees.

The ice-point (32°F) is 491.6° Rankine.

Hence any temperature in Rankine Scale,

$$\begin{aligned} T°_{\text{R}} &= (t°_{\text{F}} + 491.6 - 32) \\ &= (t°_{\text{F}} + 459.6). \end{aligned}$$

We have so far considered ice-point and steam-point as the fixed data for standardisation of a temperature scale. But for very high or very low temperature measurements other fixed points are to be accepted, such as sulphur point (b. pt.) or gold point (m. pt.). For low temperatures, the boiling point of oxygen is the fixed point.[1]

The use of two fixed points namely f.pt. and b.pt. of water was found somewhat unsatisfactory. In 1939, Giauque proposed a scale based on one *standard fixed point* and it should be *triple point of water* where ice, water and vapour would co-exist. In 1954, this proposal was agreed to by the International Committee of Weights and Measures. If T be the unknown temperature of a gas whose pressure is p, and if p_θ be the pressure at the temperature (θ) of the triple point of water, their

$$\frac{T}{\theta} = \underset{Lt\ p_\theta \to 0}{\left(\frac{p}{p_\theta}\right)_{\text{const volume}}} \qquad \text{or} \quad T = \theta \underset{Lt\ p_\theta \to 0}{\left(\frac{p}{p_\theta}\right)_v}$$

The temperature of the triple point of water was given the arbitrary value of 273.15° in order to make the degree in this scale the same as a centigrade degree.

---

[1] For detailed discussion of measurement of temperature, consult Saha & Srivastava's 'A treatise on Heat'.

1.4. Work, Energy and Heat

If an object, say a table, is pushed by the hand, it may be displaced from its original position. We consider this as a mechanical work (or simply, work) done by mascular effort. In fact, whenever the application of a force causes a displacement of a system, mechanical work is done. The magnitude of the work is measured by the product of the force and the displacement caused. Thus, work

$$W = F \times \triangle l$$

where F is the force and $\triangle l$ is the displacement caused. The lifting of a weight, the expansion of a gas by moving out a piston, the winding or unwinding of a spring, the turning of the blades of a wheel, are common instances of such mechanical work. The performance of the work need not necessarily be always achieved by mascular effort. The work may be produced in diverse ways. If a quantity of electricity Q is transported along a wire under an electromotive force E, then we consider this as electrical work,

$$W = E \times Q.$$

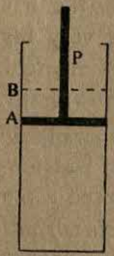

Fig. 1*d*

In thermodynamics, however, the work involved by the interaction of one part on another within a given system is not recognised. An example may be helpful. Suppose a mixture of hydrogen and oxygen is enclosed in a cylinder with a piston. The work in the diffusion process of the two gases within is not usually taken into consideration. But if the mixture as a whole expands pushing out the piston from position A to B, then work is done by the gas-system (Fig. 1*d*),

$$\begin{aligned} W &= F \times \triangle l, && (\triangle l = \text{AB}) \\ &= \text{p} \times \text{a} \times \triangle l, && (\text{a} = \text{cross section of the piston}) \\ \text{or } W &= P \times \triangle v \end{aligned}$$

where P is the pressure on the piston and $\triangle v$ is the increment in volume ; *i.e.* a.$\triangle l$.

The usual convention in thermodynamics is that *the work done by a system is positive*, whereas *the work done on the system is negative*.

To be more precise in the 'concept of work' it would be convenient to recall here a few relevant facts of experience.

Heat generated by the burning of coal ultimately enables the steam-engine to pull the train, *i.e.*, to perform work. Conversely, the mechanical work spent in rubbing two blocks of ice or in the boring of a cannon generates large quantities of heat. There is thus an intimate relation between heat and work, one can yield the other. We need not at the moment enter into the quantitative relation between the two.

An object A placed at a certain height and tied to a weight over a pulley would lift the latter when the object A descends to the surface of the earth. We state that the body A at the higher level possesses potential energy at the cost of which the work of lifting the weight is being performed (Fig. 1*e*).

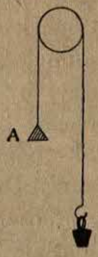

Fig. 1*e*

Electricity passed through a circuit may be made to produce the rotation of the armature of a motor used for lifting a weight or winding a spring. Conversely, the work done in turning the blades of a turbine would generate electricity. This is an instance of the conversion of electrical energy into work or vice versa. On the other hand, electricity led through a resistance would produce heat.

In a chemical reaction, say between zinc and copper sulphate, large amounts of heat are produced. The same chemical change carriedout in a voltaic (Daniell) cell, would provide electrical energy instead of heat. Here the chemical energy is being converted into heat or electrical energy. Numerous such illustrations may be cited.

Broadly speaking, two facts emerge out of these. Firstly, the different systems possess something (really the energy) which can yield work; and secondly, all these different kinds of energy are interconvertible. Energy should therefore be defined as a *property which can be transformed into or produced from work.*

In the various natural phenomena, energy manifests itself in different forms, such as, mechanical, chemical, radiant, electromagnetic, surface energy etc.

From these definition of energy, work itself becomes equivalent to energy and is an observable manifestation. In fact, different forms of energy are often expressed in terms of work.

Heat, obviously, is another form of energy since it can yield work or can be produced from work. But heat is somewhat different from other forms of energy such as electrical or chemical. All other forms of energy can be completely transformed into work, but heat cannot be wholly converted into work. Any attempt to convert the whole of a quantity of heat would affect a permanent change in the system or the neighbouring systems. There is another aspect of heat which requires attention. When two objects with different temperatures come together, one with the higher temperature loses heat energy and the other gains it. That is, energy in the form of heat flows from a higher to a lower temperature. Hence, *heat is energy in transit*. Only during the process of flow we are conscious of this form of energy. But when the flow ceases, we do not speak about the heat present in a body. 'Heat in a body' is meaningless. What may be present in a body is the energy. This energy, by out-flow of heat would be decreased and would be increased by in-flow of heat. Likewise, it would be incorrect to speak about 'work in a system'. The system during a physical or a chemical change only may yield us work at the expense of energy.

Measures for Energy : Energy is a scalar quantity. It has magintude but no direction. The energy of several systems is the sum of their individual energies. Units employed to measure energy are different for different forms of energy.

Work in cgs scale is measured in *ergs*. An erg is the work done when a force of one dyne acts through a length of one cm. [Dyne is the force which acting on a mass of 1 gm produces an acceleration of one cm/sec^2]

In ST units, work and other forms of energy are expressed in *joules*, where 1 joule = 10^7 ergs.

Now, work = force × displacement

= mass × acceleration × displacement

In dimensions, then, work $= m \times l \times t^{-2} \times l = ml^2t^{-2}$.

All forms of energy should have the same dimensions.

Heat is commonly expressed in terms of calories. One calorie is the amount of heat required to raise the temperature of 1 gm of water through 1°C, from 14.5°C to 15.5°C. *A mean calorie* is 1/100th of the heat required to raise the temperature of a gram of water from 0°C to 100°C. The bigger unit of heat is the kilocalorie.

Another unit is also used sometimes, called the British thermal unit (B.t.u.); it is the heat required to raise the temperature of 1 lb. of water through 1°F.

Electrical energy is measured as the product of e.m.f. (E) and the quantity of electricity transferred (Q) *i.e.* electrical energy $= E \times Q$. The unit of electrical energy is the volt-coulomb, and is the amount of energy involved in the transfer of 1 coulomb of electricity under the influence of 1 volt e.m.f.

Of the mechanical forms of energy, the kinetic energy, $\frac{1}{2}mv^2$ and the potential energy, mgh are commonly known, where v is the velocity and h is the height of a body of mass m.

The inter-relation between the different forms of energy will be considered when we shall discuss the first law.

1.5. Thermodynamic Systems

For the purpose of thermodynamic considerations, a system is any material or quantity of matter, chosen separately from the rest of the universe, enclosed by boundary surfaces. The boundaries of the system may be real or imaginary, but the existence of the boundaries is of importance in order to visualise the system distinctly from the rest of the universe. A quantity of a gas in a closed cylinder has real and defined boundaries, but when the same gas flows through a zigzag pipe, its boundaries constantly change and have to be followed in imagination as it progresses. Any other material or body, near or distant, besides the system chosen, *i.e.*, the rest of the universe is spoken of as the *surroundings*. A system and its surroundings constitute the *universe*. Usually a system would contain a definite mass of material but we may also consider systems in which known quantities of materials are introduced, or from which known quantities of materials are taken away. It is however not necessary that the systems should have any definite shape or volume. A thermodynamic system may contain one or more kinds of matter and may be homogeneous or heterogeneous in character.

Only on rare occasion, we shall consider even an evacuated space (containing nothing but electromagnetic radiations) enclosed by boundary walls as a system.

The boundary walls of a system may be of two types. The walls may allow the transmission of heat through them, into or out of the system. Such walls are *diathermal walls*. On the other hand, a system may be enclosed by boundary walls which would not permit any heat to enter into the system or to come out of the system. These walls are termed *adiabatic walls*. A liquid contained in a glass beaker may be easily heated by a Bunsen burner, the glass walls behaving as diathermal boundaries. If the liquid is kept in a silver-mirrored double-walled Dewar vessel, heat from a burner can little affect the temperature of the liquid within. The boundary walls here are adiabatic.

The systems are classified into three groups:

(*i*) A system is said to be an *isolated system*. When it is incapable of exchanging either energy or matter with the surroundings. The system would be bounded by adiabatic walls.

(*ii*) A *closed system* is one in which energy-exchange with the surroundings is possible but no mass-transfer across the boundary is permitted. It has diathermal walls.

(*iii*) In an *open system*, the transfer of both mass and energy across the boundary is possible.

Properties of a System : The physical characteristics or attributes which are experimentally measurable and which enable us to define a given system are called thermodynamic *parameters or properties* of the system. Various properties such as, composition, pressure, volume, temperature, refractive index, viscosity, surface tension, dielectric constant etc. may be associated with a system. But ordinarily, the first four properties, namely, composition, pressure, volume, and temperature of the system are of fundamental importance. Only on occassions of special consideration, any other property of the system, say surface tension, is accepted as a variable of the system.

The *four* variables or parameters of the system are generally sufficient to define the system thermodynamically. These parameters are directly experimentally measurable and do not require any assumption regarding the structure of the matter. If the system be homogeneous or of a given composition, then only three parameters (P,V,T) need be considered. We further know that the pressure, volume and temperature of a system are interrelated. In fact, for ideal or real gases, quantitative expressions, such as van der Waals equation, indicate these relations. Hence, in such cases, if any two of these three parameters be specified, the third is fixed. Thus, if pressure and temperature a system either homogeneous or of known mass and composition be known, the volume would have a fixed value. Hence it is said that the thermodynamic state of a system of given mass and composition is defined by specifying any two of the three parameters.

The properties of a system may be of two categories. Certain properties do not depend upon the quantity of matter present in the system at all. These are called *intensive* properties. Examples are pressure, temperature, viscosity, density, refractive index, etc. If a system is divided into two equal halves by a partition wall, the temperature or pressure would not change at all in any of the halves. There are other properties like mass, volume, surface area. etc. which would alter with the quantity of matter present in the system. The value of the property for the whole of a body is the sum of the values for all of its constituent parts. These are called *extensive* properties. A few cases are cited here:

System	*Intensive property*	*Extensive property*
Simple meterial system	Pressure	Volume
Electric cell	Electromotive force	Quantity of electricity
Paramagnetic system	Field strength	Magnetisation
Surface film	Surface tension	Surface area

1.6. Equilibrium

In a system left to itself, the parameters have a tendency to be uniform throughout the system.* The pressure and temperature thus become uniform at all points of the system. If different parts of the system have different pressures or temperatures, the parameters cannot be specified and the thermodynamic state of the system cannot be defined. When complete uniformity in the magnitudes of the variables is acquired, a steady condition is set and the system is said to have attained *equilibrium.*

For attainment of complete equilibrium, three different conditions are to be fulfilled.

(1) *Mechanical Equilibrium.* It is necessary that there should be no unbalanced forces existing between different parts of the system or between the system and the surroundings. When this condition is satisfied, the system is in mechanical equilibrium. If there be difference of pressure between the system and the surroundings, it would lead to displacement of the system with respect to the surroundings.

(2) *Thermal Equilibrium.* The temperatures at all parts of the system must be the same and should be identical with that of the surroundings. In case of existence of difference in temperatures, it is common experience that heat would flow from higher to lower temperature until uniform temperature is attained throughout. The system is then in thermal equilibrium.

(3) *Chemical Equilibrium.* When the composition of the

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* In a heterogeneous system, this would apply to each homogeneous part of the system.

system remains fixed and definite, the system is said to be in chemical equilibrium.

Some care is necessary to ascertain if chemical equilibrium has been attained by a system or not. Sometimes a reaction proceeds with such an infinitely slow rate that the system appears to be in chemical equilibrium, having fixed amounts of the components. The most frequently cited illustration is the system of a mixture of hydrogen and oxygen with supercooled water vapour at ordinary temperature. The reaction rate is so slow that in years even no variation of the concentrations of the components would be perceived. But that the system is not in true equilibrium is proved by the introduction of a minute spark which would immediately convert most of the mixture into water.

The mechanical equilibrium therefore refers to uniformity of pressure, the thermal equilibrium to uniformity of temperature and the chemical equilibrium to the constancy of chemical composition.

A system which satisfies all the three equilibria is said to be in *thermodynamic equilibrium.* Its composition and properties would undergo no observable change even in indefinite period of time. When a system is in thermodynamic equilibium, its properties have definite magnitudes. Whenever the system comes to that particular state of thermodynamic equilibrium, its properties will have the same magnitudes, regardless of what might have occurred to the system previously.

1.7. Processes

When one or more of the parameters of a system change, the state of the system also changes. It is said that the system is undergoing a *process.*

Now, if a system suffers a series of changes so as to come back to the initial state, the system is said to have completed a cycle. The series of processes, as a consequence of which the system reverts to its initial state is called a *cyclic process* or a *cycle.*

In a cyclic process, the system returns to its original state. Since the state of the system is defined by its parameters, these parameters (p, v, etc) must also revert to their initial values.

The changes of a system can be effected in different ways. If a system undergoes a change in such a way that the temperature throughout remains unaltered, it is called an *isothermal process.* On the other hand, the change in a thermally insulated system, enclosed by adiabatic walls which do not permit heat-exchange with the surroundings, is called an *adiabatic process.*

A process in which volume is kept constant is an *isochoric process*. If pressure remains constant the process is termed *isopiestic or isobaric*.

If a process is carried out in such a way that at every moment, the system departs only infinitesimally from an equilibrium state, the process is called a *quasistatic process*. At every instant, the system remains virtually in a state of equilibrium. We shall discuss this more thoroughly later in connection with reversible changes.

1.8. Internal Energy

We are familiar with different types of energy, such as kinetic and potential energy, light energy, thermal energy (heat), electrical energy, etc. Besides these, a system is said to possess what is called '*internal energy*', the concept of which is not so obvious.

When a gm of ice at 0°C melts it takes in 80 calories of heat (which is a form of energy). Where is this energy gone ? If the same amount of water now freezes into ice, the said 80 calories of heat are expelled. It seems the energy absorbed by ice during melting remained within the water. Again, when a paddle wheel is vigorously rotated in a mass of water, the latter gets heated. That is, mechanical energy of the rotating wheel is transformed into heat energy. Joule showed further that there is a proportionality between the amounts of heat generated and work performed.

It therefore appears that a thermodynamic system containing some quantity of matter, in virtue of its very existence, must possess a store of energy. This is sustained from other experiences in diverse *isolated* systems, e.g., (a) zinc and copper sulphate react in a Daniell cell when electrical energy is produced (b) hydrogen and oxygen mixture explode in a cylinder producing mechanical energy (c) carbon monoxide and oxygen unite producing heat energy etc. Unless the systems had inherent energy within, how could they isolated from the surroundings yield work or other forms of energy by themselves. Hence we believe that every system has within itself a definite quantity of energy. This is called the '*internal energy* or *intrinsic energy*' of the system. The internal energy of a system depends on its thermodynamic state, and hence, on the thermodynamic parameters. In this text, the internal energy of a system will always be expressed by the symbol U.

In a system of constant composition, the magnitude of U will depend upon other thermodynamic variables (P, V, T), any two of which may be regarded as independent variables (sec. 1-5). Thus,

$$U = f(P,T); \quad \text{or } U = f_1(P,V); \quad \text{or } U = f_2(V,T)$$

The internal energy thus becomes a *property* of the system entirely defined by its thermodynamic parameters. Whenever the system will be in the same thermodynamic state, its internal energy will have the same magnitude. The internal energy U is thus a single-valued function of the thermodynamic state of the system. Such functions whose magnitudes are governed only by the state of the system and nothing else are termed *characteristic functions* of the system, often called *state functions*.

It is true that, in most cases, it would not be possible to exactly evaluate the amount of the internal energy of the systems studied. That the systems possess internal energy is enough and is of vital importance in thermodynamics. Its implication would be fully realised from the First Law. The classical thermodynamics is also not concerned to find out how this internal energy is acquired or stored or structurally distributed within. The internal energy (U) is an extensive property.

From the microscopic viewpoint, the internal energy of a system is supposed to arise from varied type of motions and positional influences of the constituent molecules, such as translational motion of the molecules, rotation and vibration of atoms, electronic motions and spins, nuclear bindings, intermulecular interactions etc, etc.

The internal energy does not include any energy that the system may acquire as a result of its position or motion *as a whole*. A system, having been placed in a gravitational or electric field may acquire additional energy. That is, a system due to environmental conditions may happen to possess some extra energy. These *external energies* are not *usually* accepted as a part of the internal energy of the system.

Internal energy change : When a system changes from one thermodynamic state A to another thermodynamic state B, its internal energy U will also change. Let U_A and U_B be the respective internal energies in state A and in state B. U_A and U_B will depend on the parameters only of the two different states. Then, the change in the internal energy $U_B - U_A$, represented by ΔU, will be governed only by the magnitudes of the variables in the initial state A and the final state B. ΔU will thus be independent of the *path*, by which the transformation has been carried out. A particular change of a given system may be effected by different paths, but ΔU would be the same. To illustrate, a system of carbon and oxygen may be directly converted into carbon dioxide or through the intermediate formation of carbon monoxide, but ΔU in both the cases would be the same, provided the pressure, temperature etc. in the initial and final states be the same in both cases. There is a decrease in internal energy, i.e. U_{CO_2} is less than $(U_C + U_{O_2})$. ΔU[*] expresses the change in internal energy.

$$\begin{array}{lrr}
 & & \text{kj}\\
\text{(i)}\ \mathrm{C + O_2 = CO_2} & \Delta U = & -393.5\\
\textit{(ii)}\ \mathrm{C + \tfrac{1}{2}O_2 = CO} & \Delta U_1 = & -110.5\\
\mathrm{CO + \tfrac{1}{2}O_2 = CO_2} & \Delta U_2 = & -283.0\\
\hline
\mathrm{C + O_2 = CO_2} & & -393.5
\end{array}$$

In a *cyclic process*, the system returns to the initial state, and hence, its parameters would revert to their original values. The internal energy, therefore, assumes its original magnitude irrespective of what might have happened meanwhile or previously. The internal energy of the system is independent of its previous history but is defined by its parameters at the moment. If all the internal energy changes (ΔU) in the different stages of the cyclic process be summed up, these would vanish.

$$\Sigma \Delta U = \Delta U_1 + \Delta U_2 + \ldots + \Delta U_i + \ldots = 0$$

This is represented as, $\oint dU = 0$

The circle in the integral denotes a complete cyclic process.

State functions : It has already been mentioned that the internal energy (U) is a state function because its value depends only on the parameters of the system.

Later on, we shall come across other functions associated with the system, such as entropy, enthalpy, etc, which are also 'state functions'.

In contrast, there are thermodynamic quantities whose values depend on the way the transformation is carried out. Suppose the temperature of a mass of water is to be raised from $T_1°$ to $T_2°$. This can be accomplished in different ways. (fig 1*f*)

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[*] The symbol Δ would always indicate the change in quantity. The change is obtained by subtracting the initial value from the final value.

(*i*) Directly *q* calories of heat may be introduced (Fig. 1*f*.A).
(*ii*) A quantity of electricity may be passed through a coil immersed in the given system of water (Fig. 1*f*.B)
or (*iii*) A paddle-wheel may be mechanically rotated in the water, as in the historical experiment of Joule, by repeated lowering of a weight (Fig 1*f*.C)

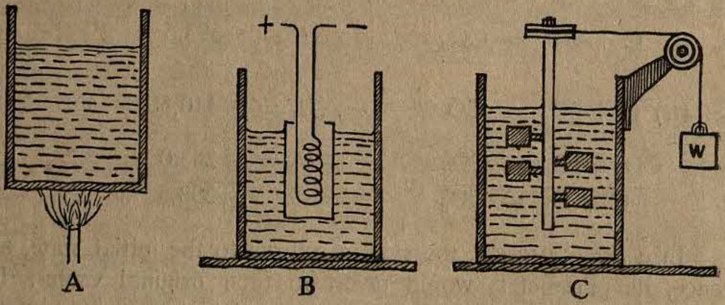


Fig. 1*f*

The change of the system in each case is the same. But

(*i*) the heat input (*q*) is nil in the process B or C but it is appreciable in the process A.

(*ii*) the performance of work (*w*) is nil in the processes A and B but it is appreciable in the process C.

Hence, the heat change *q* or the work involved *w* in a given transformation depend on the path of the change of the system. Thus, *q* and *w* do not qualify to be 'functions of state'. These are generally called '*path functions*'

1.9. Equations of State

A system of given mass and composition is thermodynamically defined by three parameters—pressure, volume and temperature. But if any two of these variables be arbitrarily chosen, the third would be automatically fixed. A system having a known pressure and volume must have a naturally defined temperature. That is, only two of the three parameters (P, V, T) are independently variable. There exists a relation between P, V and T, for a system. The relation is not precisely known for condensed systems, but for gases, such relations are well known. For an *ideal gas*, the mathematical relation is

$$PV = RT, \text{ (for 1 gm mole)} \qquad \ldots (1.1)$$

when the constant $R = 8.3149$ j per mole per degree.
If pressure be expressed in atmospheres and volume in litres, we have

$$\begin{aligned} R &= 0.08206 \text{ litre-atmospheres per mole per degree} \\ &= 1.9872 \text{ calories per mole per degree} \end{aligned}$$

The equation of state (1.1) for ideal gases is not strictly obeyed by real gases. In real gases, the equation has been empirically modified in several forms, the most common being that due to van der Waals.

$$\textit{Van der Waals eqn.,} \quad \left(p + \frac{a}{v^2}\right)(v-b) = RT \qquad \ldots (1.2)$$

Where a, b are specific constants for a particular gas, i.e. magnitudes of a, b are different for different gases.

The critical constants of a substance can be easily derived from van der Waals equation of state in terms of the constants

$$P_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27Rb} \qquad \ldots (1.3)$$

There are also other equations of state, such as,

Dieterici's eqn. $\qquad P(V-b)e^{A/RTV} = RT$

Berthelot's eqn. $\qquad \left(p + \frac{a}{TV^2}\right)(V-b) = RT$ etc

(*i*) *Coefficient of thermal expansion*, α

It is defined as the rate of change of volume with temperature at constant pressure per unit volume of the substance. This is also called *thermal expansivity*.

$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad \ldots . (1.4)$$

(*ii*) *Compressibility Coefficient*, β

It is defined as the rate of change of volume with pressure at *at constant temperature* per unit volume of the substance.

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \qquad \ldots . (1.5)$$

Relation between α and β : We know,

$$v = f(T, P)$$

Suppose a system changes its temperature by $\triangle T$ and its pressure by $\triangle p$, then

$$\begin{aligned}\triangle v &= \left(\frac{\partial v}{\partial T}\right)_P \triangle T + \left(\frac{\partial v}{\partial P}\right)_T \triangle P \\ &= \alpha V \triangle T - \beta V \triangle P \qquad \text{(from 1.4 and 1.5)}\end{aligned}$$

for an isochoric change ($\triangle V = 0$),

$$\therefore \ \alpha V \triangle T = \beta V \triangle P$$

$$\frac{\alpha}{\beta} = \left(\frac{\triangle P}{\triangle T}\right)_v = \left(\frac{\partial P}{\partial T}\right)_v \qquad \ldots (1.6)$$

(*iii*) *Isothermal Bulk modulus, B*

The isothermal bulk modulus which may be defined as the ratio of the pressure change to the change in volume per unit volume at constant temperature.

$$B = -v\left(\frac{dp}{\partial v}\right)_T \qquad \ldots (1.7)$$

$$\therefore \ B = 1/\beta \qquad \ldots . (1.8)$$

Example. Derive expressions for a and β for (*i*) an ideal gas and (*ii*) a van der Waals gas.

I. *Ideal gas.* $PV = RT$ (for 1 mole)

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad \text{and} \quad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} = -\frac{V}{P}$$

$$\left.\begin{aligned}\therefore \ \alpha &= \frac{1}{V}\cdot\left(\frac{dV}{dT}\right)_P = \frac{R}{PV} = \frac{R}{RT} = \frac{1}{T} \\ \text{and } \beta &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{V}{P}\right) = \frac{1}{P}\end{aligned}\right\} \qquad \ldots (1.9)$$

II. Van der Waals gas. For 1 mole,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

or

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT \qquad \ldots (i)$$

Differentiating with respect to T at constant P,

$$P\left(\frac{\partial V}{\partial T}\right)_P - \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{2ab}{V^3} = R$$

or

$$\left(\frac{\partial V}{\partial T}\right)_P = R \Big/ \left(P - a/V^2 + \frac{2ab}{V^3}\right)$$

$\therefore$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{PV - a/V + 2ab/V^2} \qquad \ldots\ldots (1.10)$$

Again from (*i*) above, we have, by differentiating with respect to P at constant temperature T,

$$P\left(\frac{\partial V}{\partial P}\right)_T + V - b - \frac{a}{V^2}\left(\frac{\partial V}{\partial P}\right)_T + \frac{2ab}{V^3}\left(\frac{\partial V}{\partial P}\right)_T = 0$$

or

$$\left(\frac{\partial V}{\partial P}\right)_T\left[P - \frac{a}{V^2} + \frac{2ab}{V^3}\right] = b - V \qquad \ldots (1.10a)$$

or

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{V-b}{V\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)}$$

$$= \frac{V-b}{PV - \frac{a}{V} + \frac{2ab}{V^2}} \qquad \ldots (1.11)$$

1.10. Some Simple Mathematical Formulae

A. Partial Derivatives : Suppose a quantity z is a function of two independent variables x and y, *i.e.*,

$$z = f(x, y)$$

If the co-ordinates x, y change by the amounts Δx and Δy, then the change in the value of z will be given by,

$$\Delta z = \left(\frac{\partial z}{\partial x}\right)_y \Delta x + \left(\frac{\partial z}{\partial y}\right)_x \Delta y \qquad \ldots (1.12)$$

where $\left(\frac{\partial z}{\partial x}\right)_y$ is the rate of change in the magnitude of z, when y remains constant.

Like wise, $\left(\frac{\partial z}{\partial y}\right)_x$ is the rate of change in the magnitude of z when x remains constant. These are partial derivatives.

[The subscripts x, y at the right-hand bottom indicate their constancy during the changes of the rest.]

Equations of the type (1.12) are therefore applicable to state functions, such as, internal energy, U.

$$U = f(P, T)$$

$$\therefore\ dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \qquad \ldots (1.13)$$

The equation (1.13) means that if the pressure and temperature of the system changes by amounts dP and dT respectively, the total change in internal energy dU is the sum of the two contributions. Here $\left(\frac{\partial U}{\partial P}\right)_T$ means rate of change of internal energy with pressure at constant T. So, $\left(\frac{\partial U}{\partial P}\right)_T dP$ is the magnitude of the change in U due to change of pressure alone. Similarly, $\left(\frac{\partial U}{\partial T}\right)_P$ means rate of change of internal energy with temperature at constant P. Hence, $\left(\frac{\partial U}{\partial T}\right)_P dT$ is the magnitude of the change in U due to change of temperature alone.

Such expressions would be valid in all cases of state functions. Thus.

$$V = f(T, P);\ \text{hence}\ dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

For an ideal gas, $\left(\frac{dV}{dT}\right)_P = R/P$ and $\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$

$$\therefore\ dV = \frac{R}{P}\,dT - \frac{RT}{P^2}\,dP$$

The entropy denoted by S is a state function. Hence,

$$S = f(T, V)$$

or

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,\ \text{etc.}$$

B. *Perfect Differentials:* As before, let $z = \psi(x, y)$.

It is presumed that z is a single-valued quantity such that its magnitude at any moment or in any given state is solely determined by the instantaneous values of x and y at that moment in the given state. If the variables change, the magnitude of z may change and this change dz is a *perfect* or *complete differential.* To make it clear, let us represent graphically the variables x and y along two axes at right angles (Fig. 1*g*). At the point P (with co-ordinates x, y), the magnitude of z is z_1. Again at the point Q(co-ordinates x', y') the magnitude of z is z_2. Then $dz = (z_2 \sim z_1)$ will always have the same value determined by x, y, x', y' ; dz is a perfect differential and dz is independent of the path of transformation from P to Q.

The perfect differential can be integrated to a definite value, i.e. $\int_1^2 dz = z_2 - z_1$, independent of the path of integration.

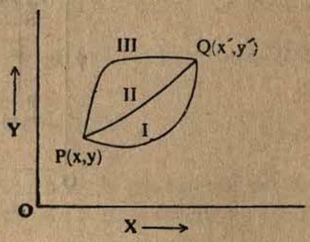


Fig. 1*g*

It is also obvious that if a change from P to Q is brought about by one path (say I) and the reverse change is effected by another path (say III), the magnitude of z will come back to the same value, defined by x, y at P. Hence for a complete cyclic process of transformation reverting to the original state,

$$\Sigma \triangle z = 0$$

$$\text{or} \qquad \oint dz = 0$$

This cannot be said of functions like heat-change or work involved. It is meaningless to say $\triangle q$ or $\triangle w$. If $\triangle w = w_2 - w_1$, or $\triangle q = q_2 - q_1$, they would mean the difference of heat (or work) between the final state and the initial state. But a system does not possess either heat q or work w initially or finally. These quantities arise only during transition. These are not properties or functions of state. Small amounts of heat or work should hence be expressed as δq and δw. These are imperfect differentials. Summation of the small quantities of heat or work would lead to the total heat-change or work involved in the transformation of the system.

$$\therefore \quad \int \delta q = q \qquad \text{and} \qquad \int \delta w = w$$

This can be considered from another direction. Let P and Q in [Fig. 1*h*] have co-ordinates (x, y) and $(x + \triangle x, y + \triangle y)$, respectively. Suppose the transition from P to Q can be effected in two ways along PRQ or PSQ.

In the path PRQ, we first change the variable x to $x + \triangle x$, y

remaining constant to reach the point R. Then x being kept constant as $(x+\Delta x)$, the variable y is altered to $(y+\Delta y)$, till Q is reached.

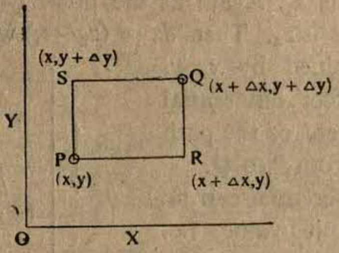


Fig. 1*h*

Then, at R, the value of z would be $z+\left(\frac{\partial z}{\partial x}\right)_y \Delta x$. So, at Q,

$$z+\Delta z = z+\left(\frac{\partial z}{\partial x}\right)_y \Delta x+\frac{\partial}{\partial y}\left[z+\left(\frac{\partial z}{\partial x}\right)_y \Delta x\right]_x \Delta y$$

Similarly, if we follow the path PSQ, the co-ordinates, at the point, S, would be x, $y+\Delta y$ and the value of z at the point S would be $z+\left(\frac{\partial z}{\partial y}\right)_x \Delta y$. So, when the point Q is reached,

$$z+\Delta z = z+\left(\frac{\partial z}{\partial y}\right)_x \Delta y+\frac{\partial}{\partial x}\left[z+\left(\frac{\partial z}{\partial y}\right)_x \Delta y\right]_y \Delta x$$

If dz is to be a perfect differential, the two expressions must be equal.

$$z+\left(\frac{\partial z}{\partial y}\right)_x \Delta y+\left(\frac{\partial z}{\partial x}\right)_y \Delta x+\frac{\partial^2 z}{\partial x \partial y}\Delta x \Delta y$$

$$= z+\left(\frac{\partial z}{\partial x}\right)_y \Delta x+\left(\frac{\partial z}{\partial y}\right)_x \Delta y+\frac{\partial^2 z}{\partial y \partial x}\Delta x.\Delta y$$

or, $$\frac{\partial^2 z}{\partial x \partial y}=\frac{\partial^2 z}{\partial y \partial x}$$

That is, if dz is a perfect differential, then $\frac{\partial^2 z}{\partial x \partial y}=\frac{\partial^2 z}{\partial y \partial x}$ ... (1.14)

Conversely, we can conclude that dz will be a perfect differential when it is found that

(*i*) z is a single-valued function depending entirely on the instantaneous values of x and y; or, (*ii*) dz between any two specified points or states is independent of the path of transition; or,

(*iii*) $\oint dz$ for complete cyclic process is equal to zero, or,

(*iv*) $\dfrac{\partial^2 z}{\partial x \partial y} = \dfrac{\partial^2 z}{\partial x \partial y}$ *i.e.*, the second differentials of z with respect to x and y carried out in either order become equal to one another.

The state functions conform to these relations.

Illustrations : (*a*) Let us take a system containing a gm-mole of an ideal gas, then, $T = f(P,V)$. Hence, by definition dT is a perfect differential. It can be proved as follows :

$$PV = RT$$

Now $\left(\dfrac{\partial T}{\partial V}\right)_P = \dfrac{P}{R}$; hence $\dfrac{\partial^2 T}{\partial V \partial P} = \dfrac{1}{R}$

Again $\left(\dfrac{\partial T}{\partial P}\right)_V = \dfrac{V}{R}$; hence $\dfrac{\partial^2 T}{\partial P \partial V} = \dfrac{1}{R}$

$\therefore$ $\dfrac{\partial^2 T}{\partial V \partial P} = \dfrac{\partial^2 T}{\partial P \partial V}$; i.e. dT is a perfect differential.

C. *Cyclic Rule*

Suppose, there is a relation between three quantities x, y and z, such that

$$f(x, y, z) = 0$$

So, we have
$$x = \psi(y, z)$$
$$y = \phi(z, x)$$

As before we can write

$$\Delta x = \left(\frac{\partial x}{\partial y}\right)_x \Delta y + \left(\frac{\partial x}{\partial z}\right)_y \Delta z \qquad \ldots (i)$$

and
$$\Delta y = \left(\frac{\partial y}{\partial z}\right)_x \Delta z + \left(\frac{\partial y}{\partial x}\right)_z \Delta x \qquad \ldots (ii)$$

Substituting (*ii*) in (*i*), we have

$$\Delta x = \left(\frac{\partial x}{\partial y}\right)_z \left[\left(\frac{\partial y}{\partial z}\right)_x \Delta z + \left(\frac{\partial y}{\partial x}\right)_z \Delta x\right] + \left(\frac{\partial x}{\partial z}\right)_y \Delta z$$

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \Delta x + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] \Delta z \ldots (iii)$$

Now, equation (*iii*) is generally true for all values of x, y and z.

Let us consider x and z as independent variables so that $\triangle x$ and $\triangle z$ may have any value.

(a) Suppose $\triangle z = 0$ and $\triangle x \neq 0$,

$$\text{then } \triangle x = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \triangle x \quad \text{(from iii)}$$

$$\text{or } \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1 \qquad \ldots (1.15)$$

$$\text{or } \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

(b) Suppose $\triangle x = 0$, and $\triangle z \neq 0$, then from (iii),

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0$$

$$\text{or } \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y = -\frac{1}{\left(\frac{\partial z}{\partial x}\right)_y}$$

$$\text{or } \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \qquad \ldots (1.16)$$

This is the 'Cyclic Rule'.

Example. Let us consider 1 gm-mole of an ideal gas, when $PV = RT$, then,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}; \; \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R}; \; \left(\frac{\partial V}{\partial P}\right)_T = \frac{-RT}{P^2}; \; \left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R}$$

Now applying (v), $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} = \frac{1}{V/\text{R}} = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}$

Again $\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \frac{R}{V} \cdot \frac{P}{R}\left(\frac{-RT}{P^2}\right) = -\frac{RT}{PV} = -1$

It corresponds to the cyclic Rule.

Example. Derive the cyclic rule for a van der Waals gas.

The van der Waals eqn : $P = \frac{RT}{V-b} - \frac{a}{V^2}$

Hence $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{P-a/V^2+2ab/V^3}{R} \quad \text{(from eqn. 1.10)}$$

$$\left(\frac{\partial V}{\partial T}\right)_T = -\frac{V-b}{P-a/V^2+2ab/V^3} \quad \text{(from eqn. 1.10a)}$$

$$\therefore \left(\frac{\partial P}{\partial P}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = \frac{R}{V-b} \times \frac{(P-a/V^2+2ab/V^3)}{R}$$
$$\times \left(-\frac{V-b}{P-a/V^2+2ab/V^3}\right) = -1.$$

Example: Suppose H and G are two state functions associated with a system having variables P,V,T and S. It is further found that the perfect differentials

(a) $dH = VdP + TdS$ and (b) $dG = VdP - SdT$

Show that (i) $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ and. (ii) $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

(i) Now, $dH = Vdp + TdS$, hence

$$\left(\frac{\partial H}{\partial S}\right)_P = T \;;\; \text{and so,} \; \frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial T}{\partial P}\right)_S$$

again, $$\left(\frac{\partial H}{\partial P}\right)_S = V \;;\; \text{and so,} \; \frac{\partial^2 H}{\partial S \partial P} = \left(\frac{\partial V}{\partial S}\right)_P$$

But dH is an exact differential, by (eqn 1.14), $\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P}$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

(ii) $dG = VdP - SdT$, hence

$$\left(\frac{\partial G}{\partial P}\right)_T = V \;;\; \text{and so,} \; \frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial V}{\partial T}\right)_P$$

again, $$\left(\frac{\partial G}{\partial T}\right)_P = -S \;;\; \text{and so,} \; \frac{\partial^2 G}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_T$$

As dG is an exact differential, (eqn 1.14); $\frac{\partial^2 G}{\partial T \partial P} = \frac{\partial^2 G}{\partial P \partial T}$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

It is possible to convert an inexact differential into an exact differential by multiplying with a siutable quantity called *integrating factor*. An example is given here to illustrate the same.

Example: The work of expansion w of a mole an ideal gas ($PV = RT$) is given by $dw = PdV$.

$$\text{Since } PV = RT \quad \text{or} \quad PdV + VdP = RdT,$$

$$dw = PdV = RdT - VdP = RdT - \frac{RT}{P}dP$$

$$\therefore \left(\frac{\partial w}{\partial T}\right)_P = R, \text{ or } \frac{\partial^2 w}{\partial P \partial T} = 0$$

And $$\left(\frac{\partial w}{\partial P}\right)_T = -\frac{RT}{P}; \text{ or } \frac{\partial^2 w}{\partial T \partial P} = \frac{RT}{P^2}$$

So, $\dfrac{\partial^2 w}{\partial P \partial T} \neq \dfrac{\partial^2 w}{\partial T \partial P}$; i.e., dw is an inexact differential.

If $\frac{1}{T}$ is used as an integrating factor. Then,

$$\frac{1}{T}dw = \frac{R}{T}dT - \frac{R}{P}dP$$

Say $\frac{1}{T}dw = d\phi$,

So $$\left(\frac{d\phi}{dT}\right)_P = -\frac{R}{T^2}; \text{ or } \frac{\partial^2 \phi}{\partial P dT} = 0$$

and $$\left(\frac{d\phi}{dP}\right)_T = -\frac{R}{P}; \text{ or } \frac{d^2 \phi}{dTdP} = 0$$

This equality shows $d\phi$ *i.e.* $\frac{dw}{T}$ is an exact differiential, though dw is not.

CHAPTER 2

THE FIRST LAW

2.1 The First Law of Thermodynamics

In the eighteenth century the caloric theory of heat was regarded as true; heat was considered as a substance contained in a body. At the close of that century Count Rumford showed that large quantities of heat are produced during the boring of a cannon without any loss in the heat capacities of the materials bored. Indeed he made an estimation of the heat produced by the power exercised by a horse. Soon after, Davy showed that rubbing of two blocks of ice could melt the same. It took however a few more decades to make complete realisation of the significance of these observations. In the early years of the last century it came to be generally believed that heat was a form of energy and heat and work are interchangeable, *i.e.*, heat can be produced at the expense of work or *vice versa*. Mayer, a German physician, was probably the first to announce in an obscure journal that there is a quantitative relation between the two forms, heat and work, when interchange takes place. From some crudely arranged experiments in those early days, he could even suggest an astonishingly accurate value of the equivalence between the two forms of energy.

Meanwhile Joule had carried out very thorough and elaborate investigations on this problem and clearly demonstrated from his experiments that the same quantity of heat would always be produced by the performance of a given amount of work, irrespective of the nature or process in which the work is performed or the substance used in the performance. In other words, there is a strict quantitative relation between the work spent and the heat produced.

Joule in his experiments, carried out the performance of work in diverse ways. The work was done by (*a*) agitating paddle wheels in a mass of water or mercury, (*b*) rubbing iron rings under mercury, (*c*) compressing air in narrow tubes, (*d*) passing electricity through a wire of known resistance, etc. The heat produced was measured from the specific heats of the materials used and the rise of temperature due to friction or passage of electricity.

For the production of unit quantity of heat (measured in calories), it would be necessary to perform a definite amount of work (measured in joules). Hence , if

$$x \text{ calories of heat } \equiv y \text{ joules of work}$$
$$nx \text{ calories of heat } \equiv ny \text{ joules of work}$$

There is a constant proportionality between the amounts of heat and work. So,

$$w = Jq$$

where J is the constant of proportionality. J is the amount of work required to produce unit quantity of heat and is called the *mechanical equivalent of heat.*

The value of J initially determined by Joule was 4.155 joules per calorie. Later on, many other workes, Rowland, Callender and Barnes, Laby and Hercus, Osborne, Stimson et al, carried out the determination of J with great precision. The present-day accepted value ;

$$J = 4.1858 \text{ joules per calorie}$$

This relation between heat and work, which is the origin of the first law, may be enunciated as "*If or whenever, heat is obtained from work, the amount of heat produced is proportional to the work spent or conversely, if heat is transformed into work, there is a proportionality between the work obtained and the heat disappeared.*"

Many instances have been cited earlier (Sec. 1.4) to show that not only heat can be converted into work but different forms of energy are all interconvertible into one another. A given quantity of electrical energy, comparatively easily measurable, was found to be equivalent to a definite amount of heat or mechanical work. It was soon realised that such equivalence did not only exist between heat and work but between any two forms of energy. And if

$$x \text{ units of energy } A \equiv y \text{ units of energy } B$$

then $$mx \text{ units of energy } A \equiv my \text{ units of energy } B.$$

The proportionality between quantities of two given forms of energy is universally constant and the constancy of the proportionality is the essence of the first law.

Helmholtz gave a clear expression of this experimentally realised experience. He stated that *the different forms of energy are interchangeable but when a quantity of one kind of energy disappears an equivalent amount of another kind makes its appearance.* This is a more general statement of the first law of thermodynamics. Since the disappearance of an amount of energy causes appearance of an equivalent amount of energy of another form, neither more nor less, we are compelled to accept that *energy cannot be completely annihilated nor can it be created from nothing.* Clausius, therefore, enunciated that varied changes and transformations might occur but the *total energy of universe must remain constant.* Hence, the first law of thermodynamics is really the **law of conservation of energy.**

Another aspect of this principle need also be considered. For a long time, all human efforts to construct a machine or device, which working in a cyclic fashion would yield work without any expenditure of energy failed and it was firmly believed that the creation of such a machine would be impossible. A machine satisfying this requirement is said to be performing *prepetual motion of the first kind.* But the creation of a perpetual motion machine of the first kind is an impossibility. That is, it has never been found possible to produce an unending supply of work by a method that leaves no change in any system.

Let us assume, for the sake of argument, that the equivalence between heat and work is not maintained. Suppose a machine converts w units of work into q calories of heat. Further, suppose, functioning in the reverse direction, the machine transforms q' calories of heat into w units of work, and say $q > q'$. In the reverse process q' units of heat yield w units of work

Hence, q units of heat yield $w(q/q')$ units of work. That is, if the whole of heat (q) generated in the forward process be reconverted into work, we shall obtain $w(q/q')$ units of work. There is thus a net gain of work $= w(q/q') - w = w(q-q')/q'$, which is a positive quantity. In other words, work is produced with no expenditure. That is, perpetual motion of the first kind is achieved, which is contrary to experience. The equivalence between two forms of energy is thus obvious.

In the thermal processes in the stars or in atomic reactors, Einstein's equation is to be invoked, $E = mc^2$ and the laws of conservation of mass and energy have to be combined.

Experiments, like those of Joule, have revealed to us another universal experience of great importance. Consider a constant volume fluid system, bounded by adiabatic walls, which is to be raised in temperature from T_1 in state A to T_2 in state B. This can be achieved at least in two ways.

In the first method a paddle-wheel is made to rotate in the fluid by allowing a weight to drop through a height h [Fig 2*a*(*i*)].

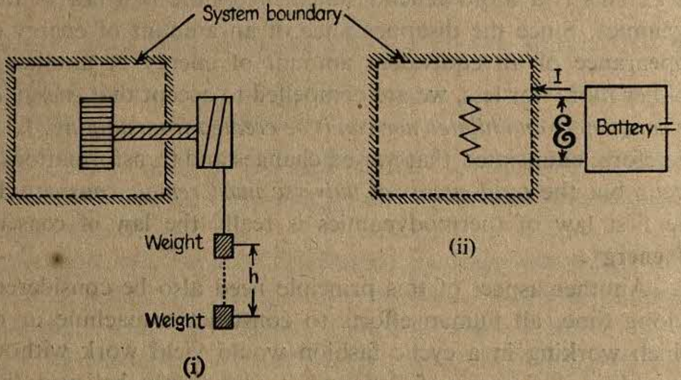


Fig. 2*a*. Work done on an adiabatically closed svstem

This is continued till the specified change from state A to state B takes place. The adiabatic work done on the system is measured by *mgh*, where *m* is the mass of the load used.

In the second method, current is passed through a resistance kept immersed in the fluid of the system and this is continued until the temperature is raised from T_1 to T_2. Here again, the adiabatic work is measured as *Eit* where *E* is the voltage, *i* is the current passed for time *t* [Fig 2*a* (*ii*)].

It is found that for the given transformation of the system from state A to state B, the adiabatic work required is the same in both the methods ; *i.e.* $mgh \approx Eit$. The work is also the same if any other process be employed to effect the said transformation. This experience may be stated as :

"*In the adiabatic transformation of a closed system, the work is the same for all possible paths from a given initial state to a final state*" or, it may be said, "*work carried on a closed adiabatic system depends on the initial and final states of the system and is independent of the path of transformation.*"

This is universally true and is regarded as an operational statement of the *First Law of Thermodynamics.*

It is obvious that there is a state function or property of the system whose change during the transformation is independent of the path and is measured by the amount of the adiabatic work involved. This property has been called *internal energy U* as mentioned in sec 1.8. In fact, the first law gave birth to the concept of internal energy. If U_2 and U_1 denote the internal energy of the system in the final and initial states, then

$$\triangle U = U_2 - U_1 = -w_{\text{adiabatic}} \quad \ldots (2.1)$$

The negative sign is introduced to indicate that work is done on the system. The work done by a system, and hence received by the surroundings, is positive. Any form of energy other than heat which would leave or enter into a system is categorically included in the term 'work'.

The increase in the internal energy of a system is regarded as positive and its decrease negative.

Algebraic formulation. Consider a system in a state A having an internal energy U_A undergoing a change to a state B. During the transformation (physical, chemical or mechanical) let the system absorb a quantity of heat q (say), then the net amount of energy of the system would become $q + U_A$. In the process of transformation, the system might have also performed some work w, electrical, mechanical or of any other type. If U_B be the internal energy of the system at state B, then the net energy after transformation would amount to $U_B + w$.

From the principle of conservation of energy, we clearly see

$$q + U_A = U_B + w$$

The heat entering into a system *i.e.*, gained by the system is conventionally regarded as positive and so heat lost by the system to the surroundings is taken as negative.

We see then, $q = U_B - U_A + w = \triangle U + w$

Or, for an infinitesimal change,

$$\delta q = dU + \delta w \ldots\ldots \quad \ldots (2.2)$$

That is, heat taken up by a system would be equal to internal-energy increase of the system plus the work done by the system. This is the algebraic statement of the First Law.

We know U depends only on the state of the system, hence its change dU for a given process is independent of the path of the change. We also know that q, the heat supplied or w the work obtained depend upon the path of the change. We therefore use different symbols to express the infinitesimal changes for internal energy (dU) and for heat-change and work term (δq, δw).

A few comments may be made on this equation.

(*a*) If the system is an isolated one, so that there is no heat exchange with surroundings, *i.e.*, in an adiabatic process, $\delta q = 0$.

$$\therefore\ dU + \delta w = 0, \qquad \text{or } \delta w = -dU$$

The work performed, irrespective of its nature, by an isolated system will be equal to the internal energy decrease.

The first law may then be stated as the *algebraic sum of the changes in energy is zero in any isolated system.*

(*b*) In a cyclic process, $\oint dU = 0$

Hence, $$\oint \delta q = \oint dU + \oint \delta w$$

or $$\oint \delta q = \oint \delta w, \textit{ i.e. } q = w$$

The total work obtained is equal to the net heat supplied and no excess work can be obtained. Thus, it establishes the impossibility of the perpetual motion of the first kind, which is our experience.

(*c*) In a non-isolated system, permitting heat-transfers with the surroundings, the system gains heat (δq) and preforms work (δw). For the system,

$$dU = \delta q - \delta w$$

If we consider the surroundings only, it loses δq amount of heat but recives δw units of work. The internal energy change of the surroundings will then be

$$dU' = \delta w - \delta q$$

Therefore $$dU = -dU'$$

The gain in internal energy of the system is counterbalanced by the loss in the same of the surroundings, or,

$$dU + dU' = 0$$

The net change in the internal energies of the system and the surroundings taken together would be nil.

We often require different forms of energy for different purposes. We need electrical energy for the light-bulb but mechanical energy for driving a car or a train. This necessitates conversion of one kind of energy into another. The transformation into the desired form may not often be directly done. For example, coal contains inherently a lot of internal energy. During burning this energy functions as chemical energy and yields heat. The heat (may be partly) is converted, by radiation, conduction, etc. into the mechanical energy of steam, which moves the engine to pull a train. Or, the mechanical energy thus produced may be made to run a generator to produce electrical energy to be used for different purposes. The electrical energy can also be made to charge a storage cell and is thus locked up in the chemical form. That means, some energy originally present in the coal is in the storage battery now. It may be questioned as to how the coal acquired the chemical energy. The radiations from the sun were picked up in the remote past by the living plants in a process called photosynthesis converting a portion of the radiant energy into chemical energy. These plants by continuous process of thermal and pressure changes went beneath the soil to be transformed into coal and petroleum. The origin is then the solar radiation. We believe that the source of all terrestrial energy is the Sun.

The practical importance of the first law is directly realised when we remember the constancy of proportionality between two forms of energy. Could we have the electrical heating or lighting system in the house if the same bulbs and the fans would consume different amounts of energy at different times? Can we imagine the chaos that would be created in our physiological system if the same amount of the same food would produce during oxidation different quantities of heat within under identical conditions? It is because of the knowledge of the work that is necessary to raise water from the ground floor to the top of the laboratory, we can prepare and adjust the power of the motor used for pumping water to the roof. These are but some very broad illustrations to show how the first law becomes operative in our daily work. Imagine the catastrophe that would occur in the earth's atmosphere if latent heat of vaporisation of water from sea and that of condensation of vapour into rain were not equal. The accummulated heat would cause extinction of life in a short time.

It may be emphasised here that δq and δw are inexactd efferentials. Their integrals depend upon the path. But their difference, $[\delta q - \delta w]$ behaves as an exact differential being equal to dU. That is, $\triangle U = q - w$.

2.2. Reversible and Irreversible processes

The change of a system from one state to another may occur in a *reversible* or in an *irreversible* way. In a reversible process, the change of the system is allowed to happen slowly in minute quantities until the whole of the specified change is achieved. In an ideally reversible process, the change must occur in *successive* stages of infinitesimal amounts. The small changes should be carried out in such a way that throughout the transition, the system must maintain virtual thermodynamic equilibrium at all the small stages. The reversible change is hence often called a **quasistatic process.** In such a process, all state functions alter so slowly that the system is at all times in an equilibrium state. The important characteristic of this process is that the process can be stopped and reversed by making an infinitesimal change of its parameters.

Moreover, a reversible process must be such that if the system change in the opposite direction back to the initial condition along the same path, the magnitudes of the changes of the thermodynamic quantities in the different stages will be the same as in the forward direction but opposite in sign. Suppose, the expansion of a gas from volume V_1 to V_2 has been effected in 100 stages both in the forward and backward directions. Then if the heat-change be $-\delta q$ and work done be $+\delta w$ in the 10th stage in the forward process, the heat-transfer would be $+\delta q$ and work $-\delta w$ in the 91st. stage in the backward transformation.

Suppose we have a system in which heat-transfer is occurring. A reversibility of the process implies that the surroundings which delivers the heat to the system must have a temperature T_1, infinitesimally higher than the temperature T of the system. Likewise, if heat is to flow reversibly from the system at T to the surroundings, then T should be slightly above T_1, the temperature of the surroundings.

Again suppose a gas is enclosed in a cylinder with a piston and kept in a constant temperature bath. The pressure over the piston is P. The gas will expand if the pressure P is very slightly lowered to P'. Let the work of expansion be δw. If now the new pressure be raised slightly, back to P, the gas will contract. It can be shown that the work now performed on the gas during contraction will be the same as received from the system during expansion. Such a change would be regarded as a reversible one.

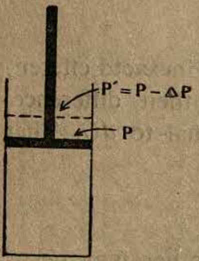


Fig. 2*b*

A truly reversible process, has to be carried out in infinitesimal amounts and, hence, would require infinite time. In practice, the small changes in a process have definite magnitudes and are thus only close approximations at the best to a true reversible process.

A strictly reversible process is thus purely a concept, nevertheless it is extremely useful in analysis of our problems of energy-changes.

An irreversible process is one which occurs suddenly or spontaneously without the restrictions of occurring in successive stages of infinitesimal quantities. The system would also not remain in virtual equilibrium during the transition. The system after undergoing a change will not have the tendency to return to the initial state by itself. If the change be reversed and the system is made to go back to the initial state, the work w in the forward direction and in the backward process would be unequal. It is important to remember that if the initial and the final states be specified, the internal energy change would always be the same, whether the process has been effected reversibly or irreversibly. In an irreversible process, since work terms (δw) in the two opposite directions are unequal, the heat-transfers (δq) would also be unequal.

Many processes occur in nature spontaneously. These spontaneous processes happen unidirectionally and certainly not in successive stages of equilibria in minute quantities of transformation. Natural processes are therefore all irreversible.

Suppose water in a beaker is heated from 20°C to 30°C by heating over a Bunsen flame. The process is irreversible, because the temperature of the flame is very high and the water near the bottom of the beaker will be more quickly heated than the rest. In consequence, convection and turbulence would start. As such, the equilibrium is disturbed and the change is not reversible.

The water from the slopes of the Himalayas flows down the Ganges into the Indian Ocean. Such natural flow of a liquid downwards is spontaneous and is irreversible. The water in the Indian Ocean will of itself never go up the hill. If the water is pushed up from the Ganges by external agencies, the work to be done far exceeds the work received during its downward flight. Hence the process is irreversible.

If the pressure over the piston of a cylinder containing a gas be reduced to zero, the gas would enormously expand immediately but work done by the system would be nil as the opposing pressure is nil. But if this gas has to be compressed to the original condition, considerable work would have to be performed on it. That is w in the two opposite directions are different and so the process is irreversible.

A gas like ammonia brought in contact with water will spontaneously be absorbed by water forming a solution, producing heat and particularly no work. Of itself, the solution would not separate back into the two components water and the gas. A lot of work has to be performed to separate these two from the solution.

Carbon, set fire to, burns in oxygen producing carbon dioxide and a quantity of heat. If the heat received thus be restored to carbon dioxide, the latter will not revert back to carbon and oxygen. The process thus carried out is irreversible.

The heat produced due to friction in the motion of two bodies is also an irreversible process. For, if the heat is supplied to the system of the two bodies, the original motion cannot be restored. Similarly, natural processes like the diffusion of two gases into one another, or flow of heat from a body at higher temperature to that at a lower temperature, are all irreversible changes.

The fact that the process is irreversible does not mean that the system cannot be restored to the original state. The water that has come down to the ocean can be taken back to the top of the hill, the carbon dioxide can be decomposed back to carbon and oxygen, etc. But such reversals would involve work by the surroundings or external agencies greater than that was obtained during the forward changes.

A change carried out naturally in an irreversible way may also be performed in a reversible fashion, but that would need some special arrangement. For example, the beaker containing water to be heated from 20° to 30°C may be placed successively in thermostats of temperatures 20.1°, 20.2°, 20.3°, 20.4° and so on, until 30°C is reached. At every stage the system must be allowed to attain equilibrium. The smaller the temperature differences of the thermostats, the more ideal would be the reversibility.

The process of irreversible solubility of ammonia gas in water may be performed in the following way to make it a reversible one. The ammonia gas may first be expanded to an infinitely large volume by reducing the pressure. If the gas at extremely low pressure be brought in contact with water extemely slowly the gas will enter the liquid. Subsequently, by gradually increasing the pressure in infinitesimal amounts the gas may be completely dissolved.

2.3. Work in Reversible Processes

(*i*) *Isothermal Expansion of a gas* : Suppose *n* moles of an ideal gas are kept enclosed in a cylinder provided with a frictionless piston (Fig. 2*c*). The cylinder is kept immersed in a large constant-temperature bath (T°K). Any change occurring to this system would be isothermal. There is a latch in the cylinder at the top (B) and the piston cannot move beyond B. The volume of the gas when the piston is at B is v_2. To start with, the gas occupies a volume v_1 and the piston is at the point A, the eqm. pressure over the piston is P_1. The aim is to expand the gas from volume v_1 to volume v_2 by reducing the pressure. This can be done in various ways. The pressure over the piston may be arbitrarily reduced to say 0, (zero), $\frac{1}{3}P_1$, $\frac{1}{2}P_1$, etc. The piston would immediately jump up.

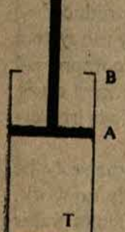


Fig. 2*c*

When the pressure is zero, the work would be *nil*. When external pressure is $\frac{1}{3}P_1$, the work would be $\frac{1}{3}P_1 (v_2-v_1)$; when the external pressure is $\frac{1}{2}P_1$, the work would be $\frac{1}{2}P_1 (v_2-v_1)$; etc. In fact, we may obtain different amounts of work from the same volume change. This shows δw is an inexact differential, w is a path function. The processes mentioned just now are all irreversible.

But the expansion can be made in a reversible fashion in the following way. Let the ext. pressure p_1 be reduced by an infinitesimal amount dp, when a minute volume-increase equal to dv would occur. The work done by the system for this small expansion would be $(p_1-dp)dv$, which is equal to p_1dv (the product of infinitesimals $dp.dv$ being negligible). The new pressure is again reduced infinitesimally be dp, a little more expansion would occur involving work output equal to $p'dv$. In this way by infinitely large number of successive minute steps, the gas would expand from volume v_1 to v_2 under quasistatic condition. This indeed is a reversible process. Let the eqm. pressure of the gas when volume is v_2 is p_2 (temp. remaining constant throughout).

The total work done by the gas is the summation of all the minute quantities of work, hence

$$w = \int_{v_1}^{v_2} (p_{ex}-dp)dv \approx \int_{v_1}^{v_2} p_{ex}dv = \int_{v_1}^{v_2} pdv$$

p_{ex} the pressure over the piston varies *quasistatically* from p_1 to p_2. Since the gas is an ideal one, $p = nRT/v$,

$$w = \int_{v_1}^{v_2} \frac{nRTdv}{v} = nRT\ln\frac{v_2}{v_1}$$

The gas being ideal, at const temp., $v_2/v_1 = p_1/p_2$

$$w = nRT\ln\frac{v_2}{v_1} = nRT\ln\frac{p_1}{p_2} \qquad \ldots (2.3)$$

For 1 gm. mole of gas, $w = RT\ln\frac{v_2}{v_1} = RT\ln\frac{p_1}{p_2}$ . . . (2.3*a*)

This work is necessarily the product of the pressure and the volume-change. The volume-change is (v_2-v_1). Hence the greater the magnitude of the pressure, larger will be the work given by the system. If the pressure over the piston were made greater than (p_1-dp), there would have been no expansion. Hence, if we want to have the expansion as desired, (p_1-dp) is the maximum pressure that could be applied. So, the work obtained in eqn 2.3 is the *maximum*. If the pressure over the piston were made appreciably less instead of infinitesimally smaller than p_1, the available work would be evidently less than that obtained above (eqn 2.3) and the process would also be more irreversible. We are therefore led to conclude that the work done by the system in the reversible process is the maximum and greater than that in the irreversible process.

Isothermal compression of the gas : We may now attempt a compression of the previous expanded gas from volume v_2 to the volume v_1 at constant temperature (T°K). To make the change reversible, it would be necessary to increase the external pressure in successive stages of infinitesimal quantites. When the pressure is made (p_2+dp), there would be a small contraction dv, the work to be done is $(p_2+dp)\,dv \approx p_2dv$. This process may be repeated slowly and in each stage, work to be done would be pdv. The net work to be done on the system,

$$w = \int_{v_2}^{v_1} pdv = \int_{v_2}^{v_1} nRT\frac{dv}{v} = nRT\ln\frac{v_1}{v_2} = -\,nRT\ln\frac{v_2}{v_1}$$

$$= -\,nRT\ln\frac{p_1}{p_2}. \qquad \ldots (2.4)$$

If the pressure applied for compression, were greater than (p_2+dp) the work performed on the gas would have been larger for the same amount of compression. It is thus seen that the work given in eqn (2.4) is the *minimum* that would have to be done on the system to achieve the specified contraction. It is also observed that in isothermal reversible expansion and in isothermal reversible compression of a gas, the work involved would be the same in magnitude but opposite in sign.

If a complete reversible cycle of expansion and contraction is carried out at constant temperature, then the net-work would be zero.

$$\Sigma w = w_{expansion} + w_{compression} = nRT\ln\frac{v_2}{v_1} + nRT\ln\frac{v_1}{v_2} = 0$$

or

$$\oint dw = 0$$

This is not only true in the expansion of a gas, but in other types of changes as well. Suppose a voltaic cell is used to perform electric work, the maximum work would be obtained if currents be drawn in exceedingly small quantities thereby reducing the emf in successively small amounts, so that emf remains as high as possible while yielding electrical work. We thus see,

(*i*) *In order to obtain maximum work from a change of a system, it must be carried out in a reversible fashion. Conversely, the work to be done on the system for a change would be minimum if the change be carried out reversibly.*

(*ii*) *The net-work in an isothermal reversible cyclic process is zero.*

The work in a reversible expansion of a gas is greater than the work obtained in an irreversible expansion. This can be easily established. Suppose n moles of an ideal gas expands reversibly from pressure P_1 to P_2, then the

$$\text{reversible work, } w_r = nRT\ln\frac{P_1}{P_2} = nRT\ln\left[1-\left(1-\frac{P_1}{P_2}\right)\right]$$

$$= -\,nRT\left(1-\frac{P_1}{P_2}\right)$$

$$= nRT\frac{(P_1-P_2)}{P_2}$$

Again, suppose the gas expands irreversibly against the constant external pressure P_2 (which is the final eqm. pressure). The irreversible work,

$$w_{ir} = P_2(V_2-V_1) = P_2\left(\frac{nRT}{P_2}-\frac{nRT}{P_1}\right)$$

$$= nRT\left(1-\frac{P_2}{P_1}\right) = nRT\left(\frac{P_1-P_2}{P_1}\right)$$

$$\therefore\ w_r - w_{ir} = nRT\frac{(P_1-P_2)}{P_2} - nRT\frac{(P_1-P_2)}{P_1}$$

$$= nRT\frac{(P_1-P_2)^2}{P_1P_2}, \text{ which is a positive quantity.}$$

Hence w_r is greater than w_{ir}.

If the system contains one gm. mole of a van der Waals' (real) gas, the work of isothermal expansion would be given by

$$w = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2}\left(\frac{RT}{V-b}-\frac{a}{V^2}\right)dV,$$

$$\text{since}\quad \left[P = \frac{RT}{V-b}-\frac{a}{V^2}\right] \qquad \text{(van der Waals')}$$

$$w = \left[RT\ln(V-b)+\frac{a}{V}\right]_{V_1}^{V_2} = RT\ln\frac{V_2-b}{V_1-b}+a\left[\frac{1}{V_2}-\frac{1}{V_1}\right] \qquad \ldots (2.5)$$

Computation of work from P-V indicator diagram : The variation of the volume of a system with pressure can also be represented graphically by the plot of pressure against volume. Pressure is plotted along the vertical and volume along the horizontal axis as in Fig. 2*d*. Such a representation becomes very useful specially in the expansion or contraction of a gas.

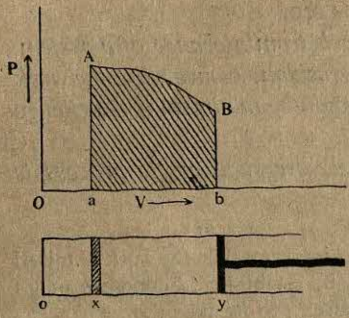
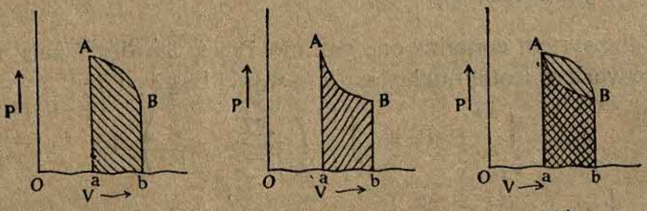


Fig. 2*d*

Imagine a cylinder containing the gas kept parallel to the *V*-axis with its closed end coinciding with the point of origin O. We may conveniently make the cross-section of the cylinder to be unity so that the distance through which the piston moves is numerically equal to the amount of volume change. To start with, let the piston be at the point x, corresponding to the point 'a' in the graph, when the pressure is aA. By reversible expansion let the piston shift to the point y, corresponding to point b, the pressure being bB. The curve AB denotes the variation of pressure during the change. The net work is $\int_a^b PdV$ and graphically it is the shaded area AabB. Such graphical representation of pressure-volume variation is called an *indicator-diagram or P-V diagram*.

The net work in a reversible cycle may also be graphically obtained (Fig 2*e*). A gas is allowed to expand, not necessarily isothermally, say, from a to b as in Fig. (i) yielding the work AabB as shaded. Subsequently the gas is compressed back to original state A by another path, the work performed is given in the shaded



(i) (ii) (iii)

Fig. 2*e*

area shown in Fig. (ii). All processes are reversible. If the two graphs be superimposed as in Fig. (iii), the difference of the two shaded areas represents the difference of work in the forward and backward changes. Hence in a cyclic process, the enclosed area within the indicator diagrams represents the net work. The area may be measured by a planimeter.

It is obvious in an isobaric process (constant pressure) the P-V curve would be a straight line parallel to V-axis. The work is given by the shaded area in Fig. 2*f*. An isochoric process is given by a line CD (Fig. 2*f*) parallel to P-axis. No work is involved as $dV = 0$.

A quasistatic isothermal expansion of a gas is typically represented by *ab* as in Fig. 2*g*. The crossed strip in the diagram gives the work when a minute expansion dv occurs. The area *abcd* stands for total work of the reversible isothermal expansion.

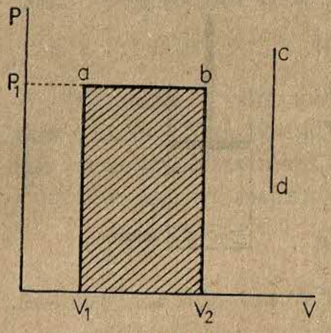


Fig. 2*f*

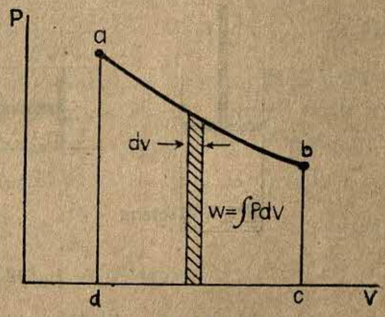


Fig. 2*g*

(*ii*) *Vaporisation of a liquid*: Consider a system containing a liquid in equilibrium with its vapour at a constant temperature and hence having constant vapour pressure P in a cylinder provided with a frictionless piston, Fig. 2*h*. If the piston is slightly raised at constant temperature, immediately a little liquid would vaporise to keep the vapour pressure constant. In this way let V_l volume of liquid be vaporised to produce V_g volume of vapour. This process takes place against constant pressure P throughout and the net volume-change of the system is $(V_g - V_l)$. Then the work performed is

$$W = P\Delta V = P(V_g - V_l) \quad \ldots (2.6)$$

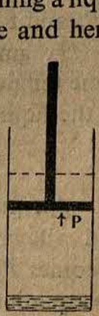


Fig. 2*h*

In most cases, V_l is negligible compared to V_g and further if the vapour is supposed to obey ideal gas laws then

$$W = PV_g = P.\frac{RT}{P} = RT \text{ (for 1 gm. mole).} \qquad \ldots (2.7)$$

Example. Evaluate the maximum work in the vaporisation of 9 gm of water at its boiling point under 1 atm.

$$W = P\triangle V = nRT = \frac{9}{18} \times 8.314 \times 373 = 1.55\text{kj}$$

(*iii*) *Addition of solvent to a solution.* If we simply add some solvent to a given solution, scarcely any work would be obtained and the process is irreversible. But a reversible work may be derived in the following way.

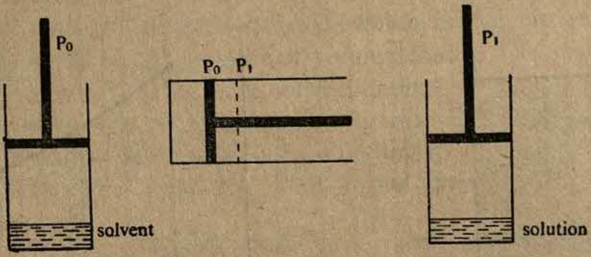


Fig. 2*i*

Consider two cylinders with pistons as before, one containing pure solvent and the other containing solution, both in equilibrium with the vapour of the solvent (Fig. 2*i*). Both are at the same temperature T°K. The vapour pressure over the solvent is P_0 and that over the solution P_1, and it is known $P_0 > P_1$. Then, let $\triangle x$ gm-moles of pure solvent be vaporised reversibly at the same temperature, the work, as in equation (2.7), neglecting volume of the liquid,

$$W_1 = P_o\triangle V = \triangle xRT$$

$\triangle x$ gm-moles of vapour is now separated from the cylinder and allowed to undergo *reversible* expansion until the pressure becomes P_1 isothermally. The work involved in this process, given by equation 2.3 assuming the vapour as an ideal gas, would be

$$W_2 = \triangle xRT \ln \frac{P_o}{P_1}$$

The vapour is now at pressure P_1. It is now introduced in the cylinder containing the solution and the piston is gradually lowered reversibly until $\triangle x$ gm-moles of vapour condense into the solution. The work, being reversible and opposite to that of vaporisation, would be

$$W_3 = -P_1 \triangle V = -\triangle xRT$$

The net work of addition of $\triangle x$ gm-moles of solvent to the solution is then

$$W = W_1 + W_2 + W_3 = \triangle xRT \ln \frac{P_0}{P_1}$$

It is presumed that such small additions of the solvent would not materially alter the concentration of the solution. If 1 gm-mole of solvent be added to a very large volume of solution, so as to make no appreciable concentration difference, then

$$W = RT \ln \frac{P_0}{P_1} \qquad \ldots (2.8)$$

If instead of pure solvent being added, a concentrated solution (concentration c_2 and vapour pressure P_2) be diluted with a less concentrated solution (concentration c_1 and vapour pressure P_1) it can be shown that net work would be

$$W = RT \ln \frac{P_1}{P_2} \qquad \ldots (2.9)$$

Assuming the solutions to be dilute and ideal ones,

$$W = RT \ln \frac{c_1}{c_2} \qquad \ldots (2.10)$$

(*iv*) *Isothermal Pressure-rise on a condensed system* : A condensed system, a solid or a liquid, when isothermally subjected to high pressure would tend to contract. The work involved is, necessarily, $\int PdV$. Since no definite equation of state is known, the evaluation is not easy as in the case of gases. But we can proceed in the following way. Since $V = f(P, T)$,

then $$dV = \left(\frac{\partial V}{\partial P}\right)_T \triangle P + \left(\frac{\partial V}{\partial T}\right)_P \triangle T$$

At constant temperature, $dV = \left(\frac{\partial V}{\partial P}\right)_T \triangle P$

The work, $W = \int_{P_1}^{P_2} PdV = \int_{P_1}^{P_2} P\left(\frac{\partial V}{\partial P}\right)_T dP,$

the pressure on the system being increased from P_1 to P_2.

Now, the coefficient of compressibility, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\text{We have, thus } W = \int_{P_1}^{P_2} (-\beta VP)dP = \beta V \int_{P_2}^{P_1} PdP$$

$$= \tfrac{1}{2}\beta V\,[P_1^2 - P_2^2] \qquad \ldots (2.11)$$

The change in V is so small that it is considered to be constant, which is particularly true in the case of solids. As such, the expression is only an approximate one.

Since $P_2 > P_1$, W is negative, *i. e.*, work is to be done by the surroundings.

(*v*) *Increase of surface area.* : A liquid has a tendency to expose as minimum as possible of its free surface and as a consequence, the surface layer is under a tension similar to that of a stretched rubber membrane. The force acting perpendicularly on a unit length on the surface is called the surface tension and is denoted by γ. If the surface area S is to be increased, work must be done by the surroundings. For any definite increase in surface from S_1 to S_2, the work would be,

$$W = -\int_{S_1}^{S_2} \gamma dS, \qquad \ldots (2.12)$$

the work will be in ergs if γ is taken in dynes/cm. and surface in cm^2.

(*vi*) *Electrical work.* Voltaic cells on completion of the circuit, would yield electricity for performance of external work and the cells would lose charge during the process. The maximum work will be obtained if the discharge is effected in infinitesimal amounts *i.e.*, against maximum opposition. This can be realised by connecting the cell against a potentiometer in such a way, that the potential differences between the points of contact A and B, is just below the e.m.f. of the cell (Fig. 2*j*). This arrangement will indeed be a very close approximation to a true reversible process in practice. If the p.d. between AB be increased, electricity will flow in

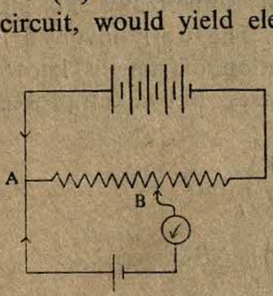


Fig. 2*j*

the opposite direction and charge the cell. The electrical work for a minute discharge, when e.m.f. (ϵ) is regarded as a constant, is $\epsilon . \triangle Z$ where $\triangle Z$ is the quantity of electricity obtained. For a definite amount of electricity being discharged

$$w = \int_{Z_1}^{Z_2} \epsilon dZ \qquad \ldots (2.13)$$

If e.m.f. be expressed in volts and Z in terms of coulobms, the work available will be in joules.

(*vii*) *Work in stretching a wire* : If a wire be subjected to a tension τ so as to cause an extension dl in length, then the work performed on it would be

$$w = -\int \tau dl \qquad \ldots (2.14)$$

The minus sign is used as work is to be done on the system to extend the wire. If τ is measured in newtons and length in meters, then the work w would be in joules.

(*viii*) *Magnetisation Work.* The field-strength H in a magnetic field is measured by the force (in dynes) exerted on a unit pole placed at the point. The unit is called an *oersted*, when a pole of unit strength placed at the point experiences a force of one dyne. This is the intensive factor in magnetisation.

The magnetisation I of a material is the magnetic moment per unit volume. The work to increase the magnetisation of a given system must be done by the surroundings, and is obtained as

$$w = -\int_{I_1}^{I_2} HdI \qquad \ldots (2.15)$$

Expressing I in pole.-cm. and H in oersteds, the work will be obtained in units of ergs.

In all cases, the work is expressed as the product of an *intensive quantity* (X_i), (often called *generalised force*), and an extensive factor (x_i), (often called *generalised displacement*). This is illustrated in the next table.

TABLE : DIFFERENT TYPES OF WORK

System	Intensive quantity	Extensive quantity	work $= \Sigma X_i x_i$
Linear Expansion	F	l	$w = \int F dl$
Hydrostatic system	P	v	$w = \int P dv$
Surface film	γ	s	$w = -\int \gamma ds$
Electric cell	ϵ	z	$w = -\int \epsilon dz$
wire stretching	τ	l	$w = -\int \tau dl$
magnetic body	H	M	$w = -\int H dM$

2.4 Calculation of work

Examples: (1) Eight grams of Helium gas occupying 4 litres at 0°C was quasistatically compressed to 1 litre at const-temperature. Assuming that the gas behaves ideally, calculate the work done.

$$n = \frac{8}{4} = 2 \text{ moles} \qquad V_2 = 1 \text{ litre} \qquad V_1 = 4 \text{ litres}$$

$$\therefore\ W = nRT\ln\frac{V_2}{V_1} = 2\times8.31\times273\times2.303\log(1/4)$$

$$= -6.3 \text{ kj}$$

The minus sign shows that work has been done on the gas.

(2) One mole of van der Waals' gas at 27°C was isothermally expanded from 2 litres to 20 litres. Calculate W. [Given $a = 1.42\times10^{12}$ dynes/cm^4 per mole^2 and $b = 30$ c.c. per mole.] From eqn. II.4, $W = RT\ln\frac{V_2-b}{V_1-b}+a\left[\frac{1}{V_2}-\frac{1}{V_1}\right]$

$$= 2.303\times8.31\times10^7\times300\log\frac{20-.03}{2-.03}+1.42\times10^{12}\left[\frac{2000-20000}{20000\times2000}\right] \text{ ergs}$$

$$= 5677\times10^7 \text{ ergs} = 5677 \text{ joules}$$

(3) For Copper at 0°C,

the bulk modulus, $B = 1.31\times10^{12}$ dynes/cm^2

the coeff. of expansion, $\alpha = 5\times10^{-5}$ per °C

and density, $\rho = 8.93$ gm/c.c.

(*i*) Calculate $(\partial v/\partial T)p$ for the metal.

(*ii*) Calculate the work involved when the pressure on 100 gm of solid copper at const. temperature (0°C) is raised from zero to 100 atmospheres.

(*i*) We know $\left(\frac{\partial v}{\partial T}\right)_p = \alpha v = \alpha/\rho = \frac{5\times10^{-5}}{8.93} = 5\times10^{-6}\ \frac{\text{cm}^3/\text{gm}}{°\text{C}}$

Thus, if expansivity coeff. be experimentally determined, we can find out $(dv/dT)_P$, which otherwise is difficult to know.

(*ii*) From eqn. 2.11, $W = \frac{1}{2}\beta v(P_1^2-P_2^2)$

$$= -\tfrac{1}{2}\frac{m}{\rho.B}P_2^2 \qquad [\because P_1 = 0, \text{ and } v = m/\rho,\ \beta = 1/B]$$

$$= -\tfrac{1}{2}\ .\ \frac{100\times(1.01\times10^8)^2}{8.93\times1.31\times10^{12}} = \frac{1.02\times10^{18}}{23.4\times10^{12}}\ \text{ergs}$$

$= 4.36\times10^{-3}$ joules.

(4) Calculate the final pressure if at constant volume 50 gm of mercury at 1 atm and 0°C be heated slowly to 24°C. Given

$\alpha = 18\times10^{-5}$ per °C, $\qquad B = 0.25\times10^{12}$ dynes/cm^2

We know, $\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V = -1$

hence, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{(\partial T/\partial P)_V} = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$

$$= -\left(-\frac{B}{V}\right)(\alpha V) = \alpha B$$

Now $dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$

At const. volume, $dP = \left(\frac{\partial P}{\partial T}\right)_V dT = \alpha B dT$

$$\therefore \int_{P_i}^{P_f} dP = \alpha B\int_{T_1}^{T_2} dT = \alpha B\int_{273}^{297} dT = \alpha B[297-273]$$

$$\therefore P_f - P_i = 24\times\alpha B = 24\times18\times10^{-5}\times0.25\times10^{12}\ \text{dynes/cm}^2$$
$$= 1080\times10^6\ \text{dynes/cm}^2$$

$$\therefore P_f - P_i = (1080\times10^6)\ /\ (1.01\times10^6)\ \text{atm.}$$
$$\approx 1070\ \text{atm.}$$

$\therefore$ Final pressure, $P_f = (1070+1) = 1071$ atm.

(5) Show that $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = 0$

(*b*) Since $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$$\therefore \left[\frac{\partial \alpha}{\partial P}\right]_T = \left[\frac{\partial}{\partial P}\left(\frac{1}{V}\right)\right]_T \left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V}\left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$= -\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V}\cdot\frac{\partial^2 V}{\partial T \partial P}$$

Again, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\therefore \left(\frac{\partial \beta}{\partial T}\right)_P = -\left[\frac{\partial}{\partial T}\left(\frac{1}{V}\right)\right]\left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]$$

$$= \frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\cdot\frac{\partial^2 V}{\partial P \partial T}$$

Hence $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial^2 V}{\partial T \partial P} - \frac{\partial^2 V}{\partial P \partial T}\right) = 0,$

for, dV is a perfect differential.

2.5. Enthalpy

The pressure and volume of a system are thermodynamic parameters ; their product PV is expressed in energy-units. The sum of the two energy-terms associated with the system, namely the internal energy (U) and the PV-energy, is universally represented by H and is called *enthalpy* or *heat-content* of the system.

$$H = U + PV \qquad \text{. . . (2.16)}$$

or in the differential form;

$$dH = dU + PdV + VdP \qquad \text{. . . (2.17)}$$

For a change under *constant pressure*,

$$dH = dU + PdV \qquad \text{. . . (2.18)}$$

Now U is a state function and P and V are themselves parameters of the state. Hence H will depend upon the parameters of the state and must be a state function. dH is thus an exact differential and will be independent of the path of the change.

Again, from the first law, $\delta q = dU + \delta w$

For a process in which the work is only mechanical, δw will depend upon P and V. Further when the change of the system occurs at constant pressure, $\delta w = PdV$

Hence, we may write

$$\delta q_p = dU + PdV \quad \ldots (2.19)$$

The subscript p is used to indicate the constancy of pressure.

Comparing equations (2.18) and (2.19),

$$dH = \delta q_p \quad \ldots (2.20)$$

or, integrating, $$\triangle H = q_p \quad \ldots (2.21)$$

Also, $$\triangle U + PdV = q_p = \triangle H \quad \ldots (2.22)$$

It shows that the enthalpy is a property of the system and its increase is equal to the amount of heat absorbed from the surroundings at constant pressure.

Since q and change in volume $\triangle V$ can be easily determined experiementally, equation (2.22) would permit the evaluation of the internal energy change ($\triangle U$).

2.6. Ideal Gases

The internal energy (U) of a system is a state function. But the nature of its dependence on the parameters of the system, say pressure or volume, is not always easy to know. That is, identification of (dU/dV), say, of a system from some measurable quantities is often difficult. A special case however arises for gaseous systems.

In the middle of the last century, Gay Lussac and, later on, Joule carried out experiments to find out changes in internal energy of a gas. The experiment was simple. As in figure $2k$, two containers A and B connected by a stop cock at the middle were taken and kept immersed in the water of a thermostat. Initially A was filled up with the gas and B was evacuated. When thermal equilibrium was established, the stop cock was opened and the gas passed into B. The flow continued until equilibrium was again reached. Since the gas expanded against zero pressure, and there

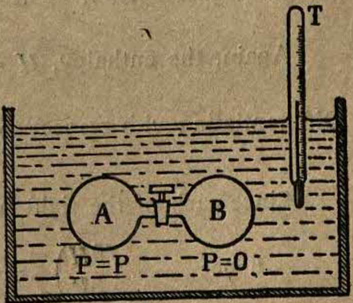


Fig. $2k$. Joules Expt, on expansion of a gas was no change in volume of the system as a whole, no work was involved, $\delta w = 0$. Very careful and repeated observations showed no change in temperature of the water in the thermostat. Hence $\delta q = 0$. Yet the volume of the gas had changed.

From the first law, we can say that $dU = \delta q - \delta w = 0$. . . . (A)

But $$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

Since $dT = 0$, $dU = \left(\frac{\partial U}{\partial V}\right)_T dV = 0$, from (A)

As $dV \neq 0$, $\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0$ . . . (2.23)

Now, $$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T = 0$$

Since for a gas $\left(\frac{\partial P}{\partial V}\right)_T \neq 0$, hence $\left(\frac{\partial U}{\partial P}\right)_T = 0$ . . . (2.24)

Subsequently it was found, specially by Joule and Thomson, that these relations are not very precise for real gases. For real gases $(\partial U/\partial V)_T$ is a small but positive quantity. The ideal gases would obey the relations mentioned above.

It is also our experience that real gases obey Boyle's Law only approximately. Boyle's Law is true for ideal gases only, *i.e.*,

(for ideal gases) $(PV)_T = k$ or $\left[\frac{\partial(PV)}{\partial P}\right]_T = 0$

Again, the enthalpy, $H = U + PV$

Differentiating with respect to P, $\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial(PV)}{\partial P}\right)_T$

Since each of the right hand terms, for an ideal gas, is zero,

hence $$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

and consequently, $\left(\frac{\partial H}{\partial V}\right)_T = 0$

Summarizing, the essential conditions for an ideal gas are

$$\left.\begin{aligned} &(i) \quad (PV)_T = \text{constant} \\ &(ii) \quad \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T = 0 \\ &\text{and also} \quad \left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial V}\right)_T = 0 \end{aligned}\right\} \qquad \ldots (2.25)$$

That is at a given temperature, the internal energy (U) and enthalpy (H) are independent of either volume or pressure of the system.

2.6a. Non-ideal Gases

In non-ideal gases, the internal energy and enthalpy alter with volume even at a constant temperature. The internal pressure is a measure of the change in internal energy per unit volume at a given temperature. For a van der Waals' gas,

$$(dU/dV)_T = an^2/v^2, \qquad \text{(for } n \text{ moles of gas)}$$

$$\therefore \qquad \int_1^2 du = \int_{V_1}^{V_2} \frac{an^2}{v^2}\, dv, \qquad (T, \text{ constant})$$

$$\text{i.e.} \qquad \triangle U = -an^2\left[\frac{1}{v_2} - \frac{1}{v_1}\right] \qquad \ldots (2.26)$$

$$\text{Again,} \qquad H = U + Pv$$

$$\text{or} \qquad \triangle H = \triangle U + (P_2v_2 - P_1v_1)$$

For a van der Waals' gas, $P = \dfrac{nRT}{v-nb} - \dfrac{n^2a}{v}$

$$\text{Hence} \quad \triangle H = \triangle U + \left[\frac{nRT \cdot v_2}{v_2 - nb} - \frac{nRT.v_1}{v_1 - nb}\right] - n^2a\left[\frac{1}{v_2} - \frac{1}{v_1}\right]$$

$$= \triangle U + nRT\left[\frac{nbv_1 - nbv_2}{(v_2 - nb)(v_1 - nb)}\right] - n^2a\left[\frac{1}{v_2} - \frac{1}{v_1}\right]$$

$$= \triangle U + n^2bRT\left[\frac{1}{v_2 - nb} - \frac{1}{v_1 - nb}\right] - n^2a\left[\frac{1}{v_2} - \frac{1}{v_1}\right]$$

Substituting for $\triangle U$ from eqn. (2.26),

$$\triangle H = n^2bRT\left[\frac{1}{v_2 - nb} - \frac{1}{v_1 - nb}\right] - 2an^2\left[\frac{1}{v_2} - \frac{1}{v_1}\right] \ldots (2.27)$$

The expression for work of expansion of a van der Waals' gas was given in sec. 2.3.

Some Numerical Examples

Example (6). Two moles of benzene (b.pt 80°C) are reversibly converted into vapour at its boiling pt. under 1 atm. The latent heat of vaporisation of benzene is 400 j/gm.

Caluclate q, w, $\triangle U$ and $\triangle H$ for the process.

Now, heat was supplied for vaporisation, hence

$$q = 400 \times 78 \times 2 \text{ joules}, \quad [M = 78]$$
$$= 62400\, j$$

Work, (w) is due to expansion at const. T and P, hence

$$w = nRT = 2 \times 8.31 \times 353\, j$$
$$= 5866.86\, j$$

$$\triangle U = q - w \qquad \text{and} \qquad \triangle H = q_p$$
$$= 62400 - 5866.86 \qquad\qquad = 62400\, j$$
$$= 56533.14\, j$$

Example (7). One mole of Argon behaving ideally was kept under a pressure of 5 atm at 27°C. The pressure is suddenly released to 1 atm and the gas expanded isothermally. Calculate q, w, $\triangle U$ and $\triangle H$ for this process.

The process is irreversible, the work against a const pressure,

$$w = P_2V_2 - P_2V_1$$
$$= P_2\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right) = nRT\left(1 - \frac{P_2}{P_1}\right)$$
$$= 1 \times 8.31 \times 300\left(1 - \frac{1}{5}\right)$$
$$= 2493 \times \tfrac{4}{5} \approx 1994 \text{ joules}$$

Since the process is isothermal,

$$\triangle U = 0, \qquad \triangle H = 0$$

And $$q = \triangle U + w = 0 + 1994 = 1994 \text{ joules}$$

Example (8). One mole of a gas is allowed to expand isothermally from a volume of 1 litre to 20 litres at 27°C. Calculate q, w, $\triangle U$ and $\triangle H$ assuming its behaviour as (*i*) an ideal gas and as a (*ii*) van der Waals' gas.

Given $a = 6.0$ atm. l^2/mole^2 and $b = 0.5$ litres / mole.

(*i*) as an ideal gas,

$$w = nRT \ln \frac{v_2}{v_1} = 2.303 \times 8.31 \times 300 \log \frac{20}{1}$$
$$= 7464 \text{ j}$$

For isothermal expansion of the ideal gas, $\triangle U = 0, \quad \triangle H = 0$

And $q = \triangle U + w = 0 + 7464 = 7464$ j (*ii*) As a van der Waals gas.

From eqn. (2.5),
$$w = RT \ln \frac{v_2 - b}{v_1 - b} + a \left[\frac{1}{v_2} - \frac{1}{v_1}\right]$$
$$= 0.082 \times 300 \times 2.303 \log \frac{20-0.5}{1-0.5} + 6 \left[\frac{1}{20} - \frac{1}{1}\right]$$
$$= 24.6 \times 2.303 \times 0.4090 - 6 \times (19/20)$$
$$= 23.17 - 5.7 = 17.47 \text{ lit-atm.}$$
$$= 1771 \text{ joules.}$$

From eqn. (2.26),
$$\triangle U = -a \left[\frac{1}{v_2} - \frac{1}{v_1}\right] = -6 \times \left(-\frac{19}{20}\right) = 5.7 \text{ lit-atm.}$$
$$= 514 \text{ joules.}$$
$$q = \triangle U + w = 514 + 1771 = 2285 \text{ joules.}$$

From eqn (2.27), for 1 mole,
$$\triangle H = bRT \left[\frac{1}{v_2 - b} - \frac{1}{v_1 - b}\right] - 2a \left[\frac{1}{v_2} - \frac{1}{v_1}\right]$$
$$= 0.5 \times .082 \times 300 \times \left[\frac{1}{20-.5} - \frac{1}{1-.5}\right] - 2 \times 6 \left[-\frac{19}{20}\right]$$
$$= 12.57 \text{ lit-atm.} = 1268 \text{ joules.}$$

2.7. Changes in internal energy (U) and enthalpy (H) with temperature : Heat Capacities

Since $U = f(V,T)$, hence
$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv$$

From the first law, $\delta q = dU + \delta w$
$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dv + pdv,$$

when the work is only mechanical.

If the system undergoes a change at *constant volume*,
$$\delta q_V = \left(\frac{\partial U}{\partial T}\right)_V dT$$

or
$$\left(\frac{\delta q}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V$$

But $\left(\frac{\delta q}{dT}\right)_V$ is the heat required to increase the temperature of the system by 1°C at constant volume and is thus the *heat capacity* (c_v) of the system at constant volume. If the system contains only one mole, then

$$\left(\frac{dU}{dT}\right)_V = \left(\frac{\delta q}{\partial T}\right)_V = C_V \text{ (for 1 mole)} \quad \ldots (2.28)$$

or $$dU = C_V\, dT \quad \ldots (2.29)$$

Hence $$\triangle U = \int_{T_1}^{T_2} C_V\, dT \quad \ldots (2.30)$$

Again $$H = f\,(P, T)$$

or $$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

At constant pressure, $$dH_P = \left(\frac{\partial H}{\partial T}\right)_P dT$$

But we know from eqn (2.20), $dH_P = \delta q_P$

$$\therefore \quad \delta q_P = \left(\frac{\partial H}{\partial T}\right)_P dT$$

or $$\left(\frac{\delta q}{dT}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

But $\left(\frac{\delta q}{\partial T}\right)_P$ is the heat required to raise the temperature of the system by 1°C at constant pressure. It is thus the *heat-capacity at constant pressure.*

$$\therefore \quad \left(\frac{dH}{\partial T}\right)_P = \left(\frac{\delta q}{\partial T}\right)_P = C_P \text{ (say, for 1 mole)} \ldots (2.31)$$

or $$dH = C_P dT \quad \ldots (2.32)$$

i.e. $$\triangle H = \int_{T_1}^{T_2} C_P dT \quad \ldots (2.33)$$

The rate of enthalpy-change at const. pressure with temperature is the heat-capacity at constant pressure. The rate of change in internal energy at const. volume with temperature is the heat-capacity at constant volume.

Let us take a gm-mole of a perfect gas. Then

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{or} \quad dU = C_V dT$$

The first Law then reduces to

$$\delta q = C_V dT + PdV \qquad \ldots (x)$$

Again $PV = RT$; hence $PdV + VdP = RdT$

i.e. $PdV = RdT - VdP$

Substituting,

$$\delta q = C_V dT + RdT - VdP$$

$$= (C_V + R)dT - VdP \qquad \ldots (y)$$

$$\therefore \quad \left(\frac{\delta q}{\partial T}\right)_P = C_V + R, \quad i.e., \quad C_P = C_V + R$$

or

$$C_P - C_V = R \qquad \ldots (z)$$

Hence for a mole of perfect gas, from (x, y and z) above,

$$\left.\begin{aligned} \delta q &= C_V dT + PdV \\ \text{also} \quad \delta q &= C_P dT - VdP \end{aligned}\right\} \qquad \ldots (2.34)$$

If a change in the gas takes place adiabatically, $\delta q = 0$, then

$$C_P dT = VdP$$

$$C_V dT = -PdV$$

$$\therefore \quad \gamma = C_P/C_V = -(VdP)/(PdV)$$

i.e., $\gamma \dfrac{dv}{v} = -\dfrac{dP}{P}$; or $\gamma \log V = -\log P + \text{const.}$

or

$$Pv^\gamma = \text{constant} \qquad \ldots (2.35)$$

2.8. Relation between C_P and C_V. (*i*) The relation between the two specific heats can be easily deduced.

(*a*) $U = f(T,V)$

$$\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \Delta T + \left(\frac{\partial U}{\partial V}\right)_T \Delta V$$

or

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots (2.36)$$

Now $C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$

$$= \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$= \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots (2.37)$$

This is applicable generally.

For a gm-mole of ideal gas, where $\left(\frac{\partial U}{\partial V}\right)_T = 0$,

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= P\left(\frac{\partial V}{\partial T}\right)_P = P \times \frac{R}{P} = R \qquad \ldots (2.38)$$

(*ii*) The difference of heat-capacities are also expressed in other forms.

$$\left(\frac{dU}{dV}\right)_T = \left[\frac{\partial(H-PV)}{\partial V}\right]_T = \left(\frac{\partial H}{\partial V}\right)_T - P - V\left(\frac{\partial P}{\partial V}\right)_T$$

Substituting it in eqn. 2.37,

$$C_P - C_V = \left[\left(\frac{\partial H}{\partial V}\right)_T - V\left(\frac{\partial P}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left[\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T - V\left(\frac{\partial P}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]\left[-\left(\frac{\partial P}{\partial T}\right)_V\right], \text{ from the cyclic rule}$$

$$= \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (2.39)$$

Again, $H = f(P,T)$, hence $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

At constant H, *i.e.* $\triangle H = 0$, using cyclic rule

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H$$

Substituting this in eqn. 2.39, we get

$$C_P - C_V = \left[V + \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H \right] \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (2.40)$$

(*iii*) It will be seen later that the rate of change of temperature with pressure at constant enthalpy ($\triangle H = 0$), is called Joule-Thomson effect and is denoted by μ.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H$$

Hence, equation 2.40, can also be expressed as,

$$C_P - C_V = [V + \mu C_P] \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots (2.41)$$

remembering $\quad C_P = (\partial H/\partial T)_P$

Variation of heat-capacities of gases with temperature : It is observed that C_P and C_V-values of gases change with temperature. From classical thermodynamics alone, we cannot derive any correlation between the heat-capacity and temperature.

From experimental measurements, some empirical relations have been developed between the temperature and heat-capacity of gases. Usually both C_P and C_V increase with temperature. The commonly used relations are,

$$C_P = a + bT + cT^2 + \ldots \qquad \ldots (2.42)$$

where a, b and c, etc. are constants.

And $\quad C_V = a_1 + b_1 T, \qquad \ldots (2.43)$

such that

$$\frac{dC_V}{dT} = \left[\frac{\partial^2 U}{\partial T^2}\right]_V = b_1 \qquad \ldots (2.44)$$

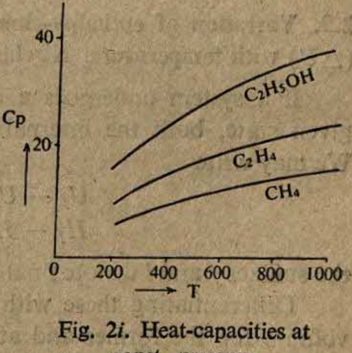


Fig. 2*i*. Heat-capacities at const. pressure.

In the table below are given the heat-capacities of some common gases and vapours.

TABLE: HEAT CAPACITIES OF DIFFERENT GASES AT CONSTANT PRESSURE IN THE TEMPERATURE RANGE 300°–1500°K

Substance	a	$b\times10^3$	$c\times10^7$
H_2	6.95	0.19	4.8
O_2	6.15	3.1	−9.23
N_2	6.52	1.25	−0.01
H_2O	7.25	2.29	+2.83
CO_2	6.21	10.4	—
CH_4	3.38	18.0	−43.0
C_2H_6	2.24	38.2	−110.4
C_6H_6	−0.41	77.6	−264.3

Example. (9) Calculate the amount of heat required to raise the temperature of a mole of nitrogen from 127°C to 327°C, the molar heat capacity of the gas is governed by the relation

$$C_P = 6.5+1.4\times10^{-3}T - 0.09\times10^{-6}T^2$$

$$\text{Heat required, } q = \int C_P dT = \int_{400}^{600} (6.5+1.4\times10^{-3}T - 0.09\times10^{-6}T^2)dT$$

$$= [6.5T+0.7\times10^{-3}T^2-0.03\times10^{-6}T^3]_{400}^{600}$$

$$= 6.5\times200+0.7\times10^{-3}(600^2-400^2)-0.03\times10^{-6}(600^3-400^3)$$

$$= 1431.5 \text{ calories.}$$

The heat-capacities of solids and liquids are generally given on unit-mass basis and are called specific heats. In these cases, C_P and C_V are not distinguished as pressure has very little influence on the specific heats of solids and liquids. The temperature has some minor effect on the specific heats of solids and liquids.

2.9. Variation of enthalpy-change ($\triangle H$) and internal energy-change ($\triangle U$) with temperature. Kirchhoff's Equation.

If a system undergoes a change from a given state to another given state, both the internal energy and heat-content would alter. We may write

$$U_f - U_i = \triangle U$$

$$H_f - H_i = \triangle H$$

the suffixes f and i denote final and initial states.

Differentiating these with respect to temperature, at constant volume for the former and at constant pressure for the latter, we have,

$$\left[\frac{(\partial\triangle U)}{\partial T}\right]_V = \left[\frac{\partial U_f}{\partial T}\right]_V - \left[\frac{\partial U_i}{\partial T}\right]_V = C_{V_f} - C_{V_i} = \triangle C_V$$

and $\left[\frac{\partial(\triangle H)}{\partial T}\right]_P = \left[\frac{\partial H_f}{\partial T}\right]_P - \left[\frac{\partial H_i}{\partial T}\right]_P = C_{P_f} - C_{P_i} = \triangle C_P$

or $\int \partial(\triangle U) = \int \triangle C_V dT$

and $\int \partial(\triangle H) = \int \triangle C_P dT$

Integrating between the limits $T°$ and 0° K we find,

$$\triangle U - \triangle U_o = \int_0^T \triangle C_V dT \qquad \ldots (2.45)$$

$$\triangle H - \triangle H_o = \int_0^T \triangle C_P dT \qquad \ldots (2.46)$$

These relations are termed Kirchhoff's equations which enable us to find out the variations of internal energy-changes or heat-content changes with temperature, from thermal data. The relations would apply to all changes, physical or chemical. It is necessary to remember that $\triangle C_V$ and $\triangle C_P$ are the differences of the heat-capacities of the system at the final and initial states.

Most of the physical and chemical changes are often carried out under constant pressure and equation (2.46) is commonly employed. We see by applying equation (2.42).

$$\triangle H_T - \triangle H_o = \int_0^T \triangle C_P dT = \int_0^T (C_{P_f} - C_{P_i}) dT$$

$$= \int_0^T (a_f + b_f T + c_f T^2 \ldots - a_i - b_i T - c_i T^2 \ldots) dT$$

$$= \int_0^T [\,(a_f - a_i) + (b_f - b_i)T + (c_f - c_i)T^2 + \ldots\,] dT$$

$$= \int_0^T (\alpha + \beta T + \gamma T^2 + \ldots) dT \qquad \ldots (2.46a)$$

$$= \alpha T + \frac{\beta T^2}{2} + \frac{\gamma T^3}{3} + \ldots \qquad \ldots (2.47)$$

where $\alpha = a_f - a_i$, $\beta = b_f - b_i$, etc.

$a_f, b_f \ldots$ and a_i, b_i etc are known from experiments.

Example (10). Calculate the latent heat of fusion of ice at −20°C if that at 0°C is 1440 cals. per mole, the specific heat of ice being 8.7 per mole.

By Kirchhoff's equation,

$$L_{-20°C} = \Delta H_{-20°C} = \Delta H_0 + \int_0^{253} \Delta C_P dT$$

$$L_{0°C} = \Delta H_0 + \int_0^{273} \Delta C_P dT$$

$$L_{0°C} - L_{-20°C} = \int_{253}^{273} \Delta C_P dT = \int_{253}^{273} [C_{P_l} - C_{P_s}]\, dT$$

$$= (18-8.7)\,(273-253) = 186$$

$$L_{-20°C} = L_{0°C} - 186 = 1440-186 = 1254 \text{ calories per mole}$$

Example (11). The heat of formation of ammonia from its elements is 11030 calories per mole at 27°C. What will be the value of the heat of formation at 1000°C? Given

$$C_{P_{(NH_3)}} = 6.2 + 7.8\times10^{-3}T - 7.2\times10^{-6}T^2$$

$$C_{P_{(H_2)}} = 6.94 - 0.2\times10^{-3}T$$

$$C_{P_{(N_2)}} = 6.45 + 1.4\times10^{-3}T$$

The reaction is, $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$; $(\Delta H_{300} = -11030 \text{ cal})$

By equation (III.19), $\Delta H_T - \Delta H_0 = \int_0^T \Delta C_P dT$

$$= \int_0^T \left[C_{P_{(NH_3)}} - \tfrac{3}{2} C_{P_{(H_2)}} - \tfrac{1}{2} C_{P_{(N_2)}} \right] dT$$

Now

$$C_{P_{(NH_3)}} = 6.2 + 7.8 \times 10^{-3}T - 7.2 \times 10^{-6}T^2$$

$$\tfrac{3}{2} C_{P_{(H_2)}} = 10.41 - 0.3 \times 10^{-3}T$$

$$\tfrac{1}{2} C_{P_{(N_2)}} = 3.225 + 0.7 \times 10^{-3}T$$

$$\Delta C_P = -7.435 + 7.4 \times 10^{-3}T - 7.2 \times 10^{-6}T^2$$

$$\Delta H_T = \Delta H_0 + \int_0^T (-7.435 + 7.4 \times 10^{-3}T - 7.2 \times 10^{-6}T^2)dT$$

$$= \Delta H_0 - 7.435T + 3.7 \times 10^{-3}T^2 - 2.4 \times 10^{-6}T^3$$

$$\therefore\ \Delta H_{T'} = \Delta H_0 - 7.435T' + 3.7 \times 10^{-3}T'^2 - 2.4 \times 10^{-6}T'^3$$

So $\Delta H_{1273} - \Delta H_{300} = -7.435(1273-300) + 3.7 \times 10^{-3}(1273^2 - 300^2)$

$$-2.4 \times 10^{-6} \times (1273^3 - 300^3)$$

$$= -1091 \text{ cal}$$

$$\therefore\ \Delta H_{1273} = \Delta H_{300} - 1091 = -11030 - 1091 = -12121 \text{ calories.}$$

Example (12). Calculate the enthalpy of vaporisation of SO_2 at −25°C if the same at its boiling pt. (−10°C) be 5950 cal/mole. Given for SO_2, $C_{p_l} = 20$ cal/mole and $C_{p_g} = 9.3$ cal/mole.

We know, $$\triangle H_{T_1} = \triangle H_{T_2} + \int_{T_2}^{T_1} \triangle C_P dT$$

$$\therefore\ \triangle H_{248} = \triangle H_{263} + \int_{263}^{248} (9.3-20.6)\, dT$$

$$= 5950 + 169.5 = 6119.5 \text{ cal/mole}$$

2.10. Adiabatic Processes

An adiabatic change, by definition, is one which does not allow any transfer of heat; *i.e.*, $q = 0$. It follows from the 1st Law,

$$\triangle U = -w,$$

or differentially, $$dU = -dw$$

If only mechanical work of expansion or contraction is involved, $dw = PdV$. Moreover, $dU = C_v dT$.

$$\therefore\ C_v dT = -PdV$$

For a system of 1 mole of an *ideal* gas, expanding adiabatically from temp. T_1 to T_2 and volume V_1 to V_2, we have

$$C_v dT = -\frac{RT}{V} dV$$

or $$\int_{T_1}^{T_2} C_v \frac{dT}{T} = -\int_{V_1}^{V_2} R\frac{dV}{V} \qquad \ldots (2.48)$$

Integrating, $$C_v \ln\frac{T_2}{T_1} = -R \ln\frac{V_2}{V_1} = R \ln\frac{V_1}{V_2}$$

or $$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_v}} = \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1};\ [\because R = C_P - C_V]$$

where γ = the heat-capacity ratio C_P/C_v.

Hence, $$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} = \text{constant}$$

i.e., $$TV^{\gamma-1} = \text{constant} \qquad \ldots (2.49)$$

Substituting T by $\frac{PV}{R}$, $$\frac{PV}{R} V^{\gamma-1} = \text{constant}$$

i.e., $$PV^{\gamma} = R \times \text{constant} = \text{constant}$$

Similarly, $TV^{\gamma-1} = T\left(\frac{RT}{P}\right)^{\gamma-1} = \text{constant}$

or $T^{\gamma}P^{1-\gamma} = \text{constant}/R^{\gamma-1} = \text{constant}$

Therefore, in adiabatic mechanical change of an ideal gas;

$$PV^{\gamma} = \text{constant}; \qquad T^{\gamma}P^{1-\gamma} = \text{constant}$$
$$\text{and} \quad TV^{\gamma-1} = \text{constant} \qquad \ldots (2.50)$$

For the adiabatic expansion of an ideal gas, $PV^{\gamma} = K'$

Also we know for isothermal expansion of the same, $PV = K$

The slope of the P-V curve will be obtained from $\frac{dP}{dV}$.

Adiabatic change; $P = K'/V^{\gamma}$; $\frac{dP}{dV} = \frac{K'}{V^{\gamma+1}}(-\gamma) = -\gamma\frac{P}{V}$

Isothermal change; $P = \frac{K}{V}$; $\frac{dP}{dV} = -\frac{K}{V^2} = -\frac{P}{V}$

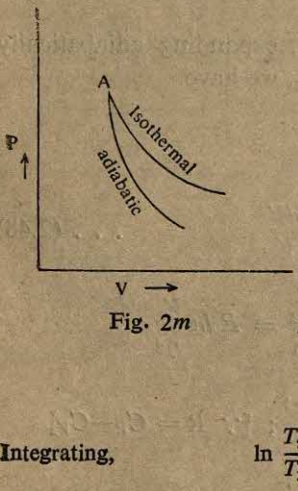


Fig. 2m

In both the changes the slope is negative. Since γ is greater than unity, the slope in the adiabatic P-V curve will be steeper than that in the isothermal one [Fig. 2m].

For a similar adiabatic change with a real (van der Waals' gas) we have

$$dU = -Pdv$$

$$\text{or} \quad CvdT = -\frac{RT}{v-b}dv\ ;$$

$$\left(\text{since} \quad P \approx \frac{RT}{v-b}\right)$$

Integrating, $\ln\frac{T_2}{T_1} = \frac{-R}{C_V}\ln\frac{V_2-b}{V_1-b}$

or $\frac{T_2}{T_1} = \left(\frac{V_1-b}{V_2-b}\right)^{R/C}$

or $T(V-b)^{R/C_v} = \text{constant}$, *i.e.* $T(V-b)^{\gamma-1} = \text{constant}$.

Putting $T = P(V-b)/R$. we have $P(V-b)\ (V-b)^{\gamma-1} = R\times\text{const}$

or $P(V-b)^{\gamma} = \text{constant}$.

Adiabatic Work. We have seen that in the adiabatic process,

$$w_{ad} = -\triangle U$$

or $$w_{ad} = -C_V\triangle T = -C_V(T_2-T_1) = C_V(T_1-T_2) \quad \ldots (2.51)$$

where T_1, T_2 are initial and final temperatures.

For 1 mole of gas, $T = PV/R$, hence adiabatic work,

$$w_{ad} = C_V\left(\frac{P_1V_1}{R}-\frac{P_2V_2}{R}\right) = \frac{C_V}{R}(P_1V_1-P_2V_2)$$

$$= \frac{P_1V_1-P_2V_2}{\gamma-1} \quad \ldots (2.52)$$

where P_1, V_1 are the initial and P_2, V_2 the final pressures and volumes.

The equation 2.52, may be rewritten as,

$$w_{ad} = \frac{P_1V_1}{\gamma-1}\left[1-\frac{P_2V_2}{P_1V_1}\right] = \frac{RT_1}{\gamma-1}\left[1-\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}\right] \quad \ldots (2.53)$$

Example 13 : A sample of a gas initially at 27°C is compressed from 40 litres to 4 litres adiabatically and reversibly. Calculate the final temperature ($C_v = 5$ cal/mole).

Assuming ideal behaviour, $C_p = C_v + 2 = 7$ cal/mole

$$\therefore\ \gamma = C_p/C_v = 7/5$$

If T be the final temp., then $\dfrac{T}{300} = \left(\dfrac{40}{4}\right)^{\gamma-1}$

or $$T = 300\times(10)^{7/5-1}, \text{ whence } T = 753.6°\text{K}$$

Example 14 : Ten liters of Helium expanded reversibly and adiabatically from 10 atm to 1 atmosphere. The final volume is 25 litres. Calculate the adiabatic work.

$$w_{ad} = \frac{P_1V_1-P_2V_2}{\gamma-1} = \frac{10\times10-25\times1}{1.66-1} = 113.6 \text{ litre-atmospheres.}$$

$(\gamma_{He} = 1.66)$

Example 15 : 1000 litres of a gas ($C_v = 3$ cal/mole) was initially at 0°C and 10 atm. Calculate the work when it undergoes adiabatic expansion (*i*) reversibly till the final pressure is 1 atm.

(*ii*) irreversibly against a constant pressure of 1 atm.

The amount of gas, $n = \frac{P_i V_i}{RT} = \frac{10 \times 1000}{.082 \times 273} = 446$ moles and $\gamma = 5/3 = 1.66$

(*i*) The final volume $V_f = \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}} . V_i = (10)^{3/5} \times 1000 = 3981$ litres

$$\therefore \text{ adiabatic reversible work } = \frac{P_i V_i - P_f V_f}{\gamma - 1}$$

$$= \frac{10 \times 1000 - 1 \times 3981}{1.66 - 1} \approx 9105 \text{ litre-atmospheres}$$

$$= 923.15 \text{ kj}$$

(*ii*) In the irreversible process, let the final volume be V' and temperature T'

$$\text{So adiabatic work, } w = P_f(V' - V_i) = P_f\left(\frac{nRT'}{P_f} - \frac{nRT_i}{P_i}\right)$$

$$= nR.P_f\left[\frac{T'}{1} - \frac{T_i}{10}\right] = nR \times 1(T' - 27.3)$$

But this work $w = -\triangle U$

$$= -nC_v.dT = \tfrac{3}{2}nR(T_i - T') = \tfrac{3}{2}nR(273 - T')$$

$$\therefore \quad \tfrac{3}{2}nR(273 - T') = nR \times 1(T' - 27.3),$$

whence $T' = 175°\text{K}.$

$$\therefore \quad w = \tfrac{3}{2}nR(T_i - T') = \tfrac{3}{2} \times 446 \times .081 \times (273 - 175)$$

$$= 2120 \text{ litre-atmospheres} \approx 215 \text{ kj}$$

Example 16: 100 gm of nitrogen gas initially at 25°C and 10 atm. expands adiabatically against constant pressure of one atmosphere. Assume the gas to be ideal and its heat capacity $C_P = 6.96$ cal/mole. Calculate the final temperature, and $\triangle U$ and $\triangle H$.

Given 100 gm N_2 = 100/28 = 25/7 gm moles, and

$$C_P = 6.96, \textit{i.e.}, C_V = 4.96, \text{ as the gas is ideal}$$

The initial pressure, $P_1 = 10$ atm.; initial temp. = 298°K, and hence the initial volume

$$V_1 = \frac{nRT_1}{P_1} = \frac{25}{7} \times \frac{.081 \times 298}{10} = 8.67 \text{ litres}$$

i.e., initial volume per gm mole, $v_1 = 2.44$ litres.

The final (constant) pressure $P_2 = 1$ atm.
Let the final temperature be T_2 and the volume V_2
Suppose also that final volume per mole $= v_2$

Then in adiabatic expansion of 1 gm-mole of the gas against constant pressure P_2 (= 1 atm), we have

$$C_V dT = -P_2 dv = -P_2(v_2 - v_1) = P_2(v_1 - v_2)$$

or $$4.96\,(T_2 - T_1) = 1(2.44 - v_2) \times 24.2 \text{ cal}$$

[1 lit. atm. = 24.2 cal]

Again $$\frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}, \text{ or } \frac{v_2}{T_2} = \frac{P_1 v_1}{P_2 \times T_1} = \frac{10 \times 2.44}{298} = \frac{24.4}{298}$$

or $$v_2 = \frac{24.4}{298} T_2$$

Substituting. $$4.96\,(T_2 - 298) = \left(2.44 - \frac{24.4}{298} T_2\right) 24.2$$

whence $$T_2 = 222^\circ\text{K}$$

∴ $$v_2 = \frac{24.4}{298} \times 222 \text{ per mole}$$

The final volume of the given sample, $V_2 = \frac{25}{7} \times \frac{24.4 \times 222}{298} = 64.3$ litres

Now $$\Delta U = -nC_V dT$$
$$= -\frac{25}{7} \times 4.96 \times (298 - 222) = -1346 \text{ cal}$$

And $$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$
$$= -1346 + (1 \times 64.3 - 10 \times 8.67) \times 24.2$$
$$= -1888 \text{ cal}$$

2-11. Determination of γ

The value of γ has been determined in various ways. A few of these methods are mentioned below:

(a) Lummer and Pringsheim and, later on, Partington used the adiabatic P-V-T relations (eqn. 250) for determining C_P/C_V *i.e.*, γ.

A 100 litre copper globe provided with a stop-cock and a manometer was filled with a gas at pressure P_1 somewhat greater than the atmospheric pressure P. A very sensitive resistance thermometer was inserted in the globe to record the temperature. The stop-cock is opened for a short while and there is an instantaneous adiabatic expansion of the gas. The pressure inside falls to P and let the temperature drop from T_1 to T (Fig 2n). Then assuming the gas behaving ideally, for a gm mole of gas,

$$P_1V_1^{\gamma} = PV^{\gamma}$$

where V_1, V are initial and final molar volumes.

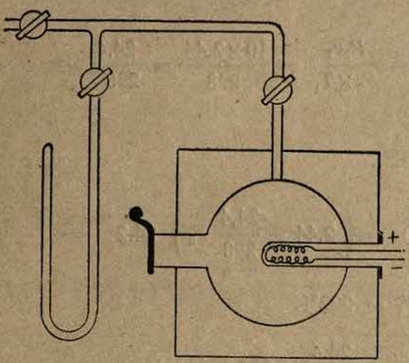


Fig 2n : Determination of γ

$$\text{Now, } \frac{P_1V_1}{T_1} = \frac{PV}{T} \text{ i.e., } \frac{V_1}{V} = \frac{P}{P_1}\cdot\frac{T_1}{T}$$

$$\text{Hence, } P_1\left(\frac{V_1}{V}\right)^{\gamma} = P$$

$$\text{or} \quad P_1\left(\frac{P}{P_1}\cdot\frac{T_1}{T}\right)^{\gamma} = P$$

$$\text{or} \quad \gamma \ln\left(\frac{P}{P_1}\cdot\frac{T_1}{T}\right) = \ln\frac{P}{P_1}$$

$$\text{or} \quad \gamma = \frac{\ln P - \ln P_1}{\ln P/P_1 - \ln T/T_1}$$

Thus the value of γ could be ascertained from the measurements of pressures and temperatures before and after the change.

(*b*) The isothermal bulk modulus (B) commonly called isothermal elasticity has been defined as $B = -v\,(\partial P/\partial v)_T$.

If $(\partial P/\partial v)$ be measured under adiabatic conditions then the value would be different. As such, the adiabatic elasticity has been defined as $B_s = -v(\partial P/\partial v)_s$

$$\text{For an isothermal process, } PV = K, \quad \text{hence } \left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}$$

$$\text{For an adiabatic process, } PV^{\gamma} = K_1 \text{ hence } \left(\frac{\partial P}{\partial V}\right)_S = -\gamma\frac{P}{V}$$

$$\text{Hence } B = V.\frac{P}{V} = P; \text{ and } B_s = V.\frac{\gamma P}{V} = \gamma P$$

$$\therefore \quad \frac{B_s}{B} = \gamma$$

Hence knowledge of isothermal and adiabatic elasticities would enable the determination of γ.

(*c*) **From the velocity of sound.** The velocity of sound (C) in a gas of density (d) and pressure P is given by the relation

$$C^2 = \gamma \left(\frac{\partial P}{\partial d}\right)_T$$

or

$$\gamma = C^2 \left(\frac{\partial d}{\partial P}\right)_T, \text{ where } \gamma \text{ is the heat-capacity ratio.}$$

In a real (Berthelot) gas, it is known that

$$d = \frac{M}{V} = \frac{MP}{RT}\left[1 - \frac{9}{128}\frac{PT_c}{TP_c}\left(1 - \frac{6T_c^2}{T^2}\right)\right]$$

Hence
$$\gamma = \frac{C^2M}{RT}\left[1 - \frac{9}{64}\frac{PT_c}{TP_c}\left(1 - \frac{6T_c^2}{T^2}\right)\right]$$

The velocity of sound (C) is measured by any standard method, say, by Kundt's tube or Dixon pipe. The standard values of critical constants of the gas are used to evaluate γ.

2.12. Steady-flow of Fluids

In the modern age of engines, jets and rockets, the flow-processes of fluids through mechanical devices have acquired great importance. The basic thermodynamic criteria in such flow-processes of fluids may be considered here.

Fluids are often allowed to flow at a steady rate through mechanical devices to perform work. In such processes, the fluids usually absorb heat from the surroundings at a steady rate and then yield work also at a steady rate. The fluid, usually enters the system at an elevation, say z_1 from a standard level, at a pressure P_1 and comes out at pressure P_2 at an elevation z_2. Let W be the work done by it to the surroundings, often called by engineers as shaft-work, and Q be the heat taken in, when mass m of the fluid steadily passes through the system. Let V_1 and V_2 be the volume of the mass m at pressures P_1 and P_2 respectively. Let also the velocity of the fluid at the entrance be x_1 and at the exit x_2 (Fig. 2*o*).

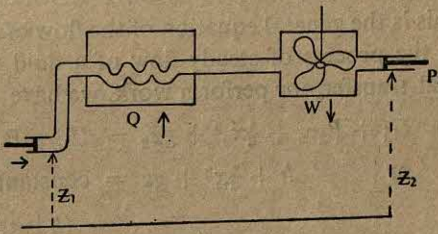


Fig. 2*o*

Then the total work performed by the fluid in the process

$$= W + P_2V_2 - P_1V_1$$

The energy associated with the system are as follows:

(1) Potential energy: at the entrance, $= mgz_1$
at the exit, $= mgz_2$
(2) Kinetic energy : at the entrance, $= \frac{1}{2}mx_1^2$
at the exit, $= \frac{1}{2}mx_2^2$
(3) Internal energy : at the entrance, $= mU_1$
at the exit, $= mU_2$.

The net energy-change is then,

$$\triangle E = mU_2 - mU_1 + \tfrac{1}{2}mx_2^2 - \tfrac{1}{2}mx_1^2 + mgz_2 - mgz_1$$

Normally in evaluating energy-changes in thermodynamic systems, potential and kinetic energies are considered as external and not taken into consideration. But in the flow of the system, part of these energies may be involved in the work out-put.
Applying the first law,

$$Q = m[U_2 - U_1 + \tfrac{1}{2}x_2^2 - \tfrac{1}{2}x_1^2 + gz_2 - gz_1] + W + P_2V_2 - P_1V_1$$

Dividing both sides by m, we can write

$$q = \omega + [U_2 + P_2v_2 + \tfrac{1}{2}x_2^2 + gz_2 - U_1 - P_1v_1 - \tfrac{1}{2}x_1^2 - gz_1]$$

where ω, v_1, v_2, q, U_1, U_2 refer to unit mass.

$$\therefore\ [U_2 + P_2v_2 + \tfrac{1}{2}x_2^2 + gz_2] - [U_1 + P_1v_1 + \tfrac{1}{2}x_1^2 + gz_1] = q - \omega$$

This is the general equation of the flow of a fluid.
In the process of steady flow of a fluid which would neither allow heat-transfer nor perform work, we have

$$U_2 + P_2v_2 + \tfrac{1}{2}x_2^2 + gz_2 = U_1 + P_1v_1 + \tfrac{1}{2}x_1^2 + gz_1$$

or $$h + \tfrac{1}{2}x^2 + gz = \text{constant}$$

(h is the enthalpy per unit mass.)

If the fluid is incompressible, $dV = 0$, and in adiabatic flow, $q = 0$, hence from the first law, $dU = 0$, *i.e.*, $U_2 = U_1$.

Therefore, in the steady adiabatic flow of an incompressible fluid, $$pv + \tfrac{1}{2}x^2 + gz = 0$$

This is called *Bernoulli's equation.*

(*i*) If the fluid is passed through fine orifice or apertures or a porous plug, often called the *throttle*, no shaft work is done and no heat transference takes place. In such a horizontal flow, $H_1 = H_2$, the condition is isoenthalpic as we see in Joule-Thomson experiment.

(*ii*) In the case of a turbine, maximum work is derived with minimum waste of kinetic energy and the process is adiabatic. In such a horizontal flow of the fluid, $H_2 - H_1 = w$.

(*iii*) In the case of a nozzle, the speed of the moving fluid changes considerably due to the change in the cross-sectional area of the flow. No external work and no heat transfer occur. Here, in horizontal adiabatic flow,

$$H_2 - H_1 = \tfrac{1}{2}(mx_1^2 - mx_2^2)$$

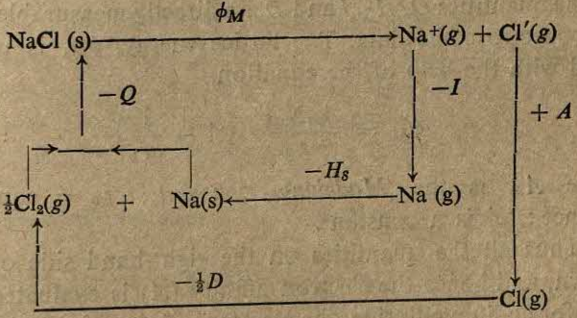
If the initial velocity x_1 is small, we may say,

$$x_2^2 = -2\triangle H/m$$

2-13. Determination of Electron Affinity : Born-Haber Cycle

An interesting application of the first law of thermodynamics made in the determination of the *electron affinity*. The electron affinity is a measure of the energy-change occurring when an electron is absorbed, such as $Cl + \epsilon = Cl^-$. This has been rendered possible by carrying out an isothermal cyclic process, known as the **Born-Haber Cycle.**

To illustrate the cyclic process let us start with crystals of sodium chloride. The cycle may begin with a mole of NaCl (crystals) which would be converted into gaseous Na^+ and Cl^- ions. These ions would then be converted into their atoms, which would reunite to form solid NaCl and the cycle would be completed. The cyclic process may be schematically represented as



where ϕ_M = lattice energy
H_S = heat of sublimation of Na
D = heat of dissociation of Cl_2
I = ionisation potential of Na
A = electron affinity of chlorine
Q = heat of formation of NaCl

Starting with a gm-mole of NaCl crystal, the process consists of converting it into gaseous Na^+ and Cl^- ions and subsequently reuniting the ions to produce back the solid NaCl. The steps in the complete cycle are as follows :

Processes	*Energy change* (*heat absorbed is positive, heat given out negative*)
(*a*) One gm-mole NaCl is converted into $Na^+(g)$ and $Cl^-(g)$ ions, absorbing lattice energy $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$	ϕ_M
(*b*) An electron is taken out from Cl^- ion and the same is accepted by Na^+ ion $Na^+ + \epsilon \rightarrow Na$	$-I$
$Cl^- - \epsilon \rightarrow Cl$	A
(*c*) Chlorine atoms are converted into chlorine molecules, giving out heat of dissociation (*D*) $Cl \rightarrow \frac{1}{2}Cl_2$	$-\frac{1}{2}D$
(*d*) Sodium atoms are condensed to the solid state $Na(g) \rightarrow Na(s)$	$-H_S$
(*e*) Chlorine is allowed to react with solid sodium atom producing the original substance, evolving heat of reaction $Na(s) + \frac{1}{2}Cl_2 \rightarrow NaCl(s)$	$-Q$

For the isothermal complete reversible cycle, net energy-change is nil. Hence

$$\phi_M - I + A - \tfrac{1}{2}D - H_S - Q = 0$$

or electron affinity, $A = I + \frac{1}{2}D + H_S + Q - \phi_M$ . . . (i)

The quantities Q, H_S, I and D are directly measurable, sometimes from spectroscopic data. The lattice energy, ϕ_M, is usually computed with the help of the equation,

$$\phi_M = \frac{A_m N_0 \epsilon^2}{r_0}\left(1 - \frac{1}{a r_0}\right)$$

where A_m is the *Madelung constant* ; r_0 = eqm. interionic distance ; '*a*' is a constant.

Thus all the quantities on the right-hand side of eqn. (i) is known, and hence the electron affinity (A) is evaluated. From the data for sodium chloride, the electron affinity of chlorine is

$$A = Q + H_S + \tfrac{1}{2}D + I - \phi_M$$

$$= 98 + 26 + \tfrac{1}{2}(58) + 118 - 184 = 87 \text{ kcal}$$

Problems

1. Explain clearly what is meant by 'internal energy'. For each of the following processes, fill in the blank spaces :

Process	q	w	U_1	U_2	ΔU
(*i*)	−10			65	−20
(*ii*)		15	−10		20
(*iii*)	25	−10		−10	

2. A simple closed system suffers a quasistatic cyclic process of three steps. Fill in the missing data in the table below :

Process	q	w	ΔU
1 ~ 2		0	50
2 ~ 3	0	−40	
3 ~ 1	−30		

3. A current of 1.00 ampere was passed through a coil having a resistance of 4 ohms for 5 minutes. The weight of the coil was 2.00 gm and heat-capacity 0.1 cal per gm per °C. It was immersed in 50 gm water in a container whose water-equivalent was 4.8 gm. The rise in temp of the system due to passage of current was 5.22°C. Find the thermal equivalent of the electric energy.
Ans. 1 cal = 4.18 joules

3.(a) An amount of work is required to reduce the volume of an ideal gas quasistatically and isothermally at 200°C. At what temperature will the same amount of work reduce isothermally the volume to a quarter of the same initial volume? **Ans.** 236.5°K

4. Calculate the work involved in the following reversible processes :
   (*i*) 5 moles of an ideal gas are heated at constant pressure from 0°C to 100°C
   (*ii*) One mole of water is heated from 0°C to 100°C at a constant pressure of 1 atm. [$\rho_{273} = 0.99984$, $\rho_{373} = 0.95834$ gm/c.c.]
   (*iii*) At N. T. P., 45 gm ice melt into water. The decrease in volume = 1.48 cc/mole
   (*iv*) One gm-atom of zinc dissolves at the anode of a Daniell cell, emf = 1.1 volt.
   (*v*) 5gm $CaCO_3$ decomposes at 327°C
   Ans. (*i*) 4.158 kj (*ii*) 7.85×10^{-4} lit-atm (*iii*) -3.7×10^{-3} lit-atm (*iv*) 212 kj (*v*) 2.52 kj

5. (*i*) 100 gm argon behaving ideally expands from 10 atm to 0.1 atm at 10°C. Calculate the heat absorbed.

(*ii*) What amount of heat will be needed to heat 200 gm NO from 27°C to 227°C at constant pressure.

$C_{p_{NO}} = 7.0 + 7.1\times10^{-3}\ T - 1.9\times10^{-6}T^2$ cal/mole.

Ans. (*i*) 8580 cal (*ii*) 8670 cal

6. A system undergoes a certain change by path I when the heat absorbed and work done are 10 Kcal and 0 ergs respectively. For the same change in state by path II, the respective quantities are 11 Kcal and 0.5 w_{max}, where w_{max} represents the work done if the change were reversibly carried out. Find the magnitude of w_{max}. (C.U. 1974) **Ans.** w_{max} = 8.4 joules

7. The restoring force, *f*, of a stretched rubber strip is given by

$$f = CT\left[\frac{L}{L_o} - \left(\frac{L_o}{L}\right)^2\right]$$

Where *L* is the length and *T* is the temperature of the strip. *C* is a constant and L_o is the length under zero force. The work $dw = -fdL$.

Show that the work attending the isothermal stretching of a piece of rubber from L_o to *L* will be

$$w = -\tfrac{1}{2}(CL_oT)\left[\left(\frac{L}{L_o}\right)^2 + 2\frac{L_o}{L} - 3\right]$$

8. Compute the maximum work when the pressure on 10 gm hydrogen is reduced isothermally at 0°C from 20 atm to 1 atm. **Ans.** 33.96 kj

9. Two litres of CO_2 (behaving ideally) at 0°C and 5 atm are expanded isothermally until the pressure is one atmosphere. Calculate *w*, *q*, $\triangle U$ and $\triangle H$. Also find out the values if the process were adiabatic ($\gamma = 1.3$). **Ans.** $w = q$ = 16.08 lit-atm. w_a = 10.3 lit-atm.

10. The molar heat of vaporisation of $H_2O\ (l) \rightarrow H_2O\ (g)$ is 9700 cal at 100°C. The molar volumes of liquid and vapour are 18 c.c. and 30.2 litres at 100°C and 1 atm. Evaluate $\triangle U$ per mole at 100°C and 1 atm. **Ans.** 37.695 kj

11. Evaluate $\triangle U$ at 500°K for the process
$Mg\ (s) + 2HCl\ (g) = MgCl_2\ (s) + H_2\ (g)$; $\triangle H = -109$ Kcal
The volume-change of solids to be ignored. **Ans.** $\triangle U = -108$ Kcal

12. One mole of TNT, $[CH_3.C_6H_2(NO_2)_3]$, on explosion produces three moles of CO and two moles of N_2.
In a constant-volume calorimeter, when 0.1135 gm TNT were exploded at 27°C, the heat evolved was 410 calories. Calculate $\triangle U$ and $\triangle H$ when 1 mole TNT explodes at 27°C. **Ans.** $\triangle U = -820$ Kcal; $\triangle H = -817$ Kcal

13. An airplane weighing 63000 Kg flies up from sea-level to a height of 8000 metres. Its engine, run with pure normal octane (C_8H_{18}), has a 30% efficiency. Calculate the fuel cost of the flight if octane sells at Rs. 3/- per litre. Given : density of octane = 0.705 gm/c.c. ; the heat of combustion of octane = 1300 Kcal/mole, (g = 981). **Ans.** Rs. 1464/-

14. Calculate the minimum work to be done when one mole of N_2, a van der Waals' gas, is isothermally compressed from 10 litres to 1 litre at 127°C [a = 1.39 atm-lit²/mole², b = 0.039 litre/mole]. **Ans.** −8.091 kj

15. 5.6 gm of Nitrogen ($C_p = \frac{7}{2} R$) at 27°C is adiabatically compressed from 10 to 5 litres. Calculate the final temperature and also the work done on the gas. **Ans.** 92.7°C, −1.38 kj

16. A real gas obeys the relation $PV = RT + a/V$ where $a = 3.6$ atm-lit²/mole². Calculate the work done when one mole expands from 0.224 litres to 22.4 litres at 127°C. **Ans.** 16.94 kj

17. The pressure of a gas is given by $P = 20/V$, where P is in atmospheres and V in litres. If the gas expands from 5 to 50 litres and undergoes an increase in internal energy by 200 cal, how much heat will be absorbed during the process? **Ans.** 1323.4 cal

18. The equation of state for NO is given by $P(V-nb) = nRT$, where $b =$ 40 c.c./mole. Calculate the maximum work when 7.5 gm of the gas expands isothermally at 47°C from 5 to 25 litres. **Ans.** 10.697 kj

19. A mole of an ideal gas ($C_v = 8.0$ cal) was initially at 0°C and 10 atm. The external pressure is suddenly reduced to 1 atm and the gas expands adiabatically against this pressure. What is the final temperature? final volume? **Ans.** 218°K, 17.9 litres

20. In an adiabatic change for an ideal gas, show that

(*a*) $C_p \log T_2/T_1 = R \log P_2/P_1$

(*b*) the work done in an adiabatic expansion.

$$w = \frac{P_i V_i}{\gamma-1}\left[1 - \left(\frac{P_f}{P_i}\right)^{\frac{\gamma-1}{\gamma}}\right]$$

21. (*a*) One mole of He at 27°C and 1 atm is adiabatically reversibly compressed to a final pressure of 10 atm. Evaluate the final temperature and also find out w, ΔH and ΔU.

(*b*) The same gas is compressed adiabatically against a constant pressure of 10 atm, the final pressure is 10 atm. Evaluate again the final temperature and the values of w, ΔH and ΔU.

Ans. (*a*) $T = 756$°K, $\Delta H = 2280$ cal, $w = -\Delta U = -1368$ cal
(*b*) $T = 1380$°K, $\Delta H = 5400$ cal, $w = -\Delta U = -3240$ cal

22. Calculate the enthalpy of vaporisation of SO_2 at 25°C if the same at its b.pt. (−10°C) be 5950 cal/mole. Given the molar heat capacities $C_{p(l)} = 20.6$ cal/mole, $C_{p(g)} = 9.3$ cal/mole **Ans.** 6119.5 cal

23. For the reaction $CO + \frac{1}{2}O_2 = CO_2$; $\Delta H = -67650$ cal at 25°C. Find out ΔH of the process at 100°C. Given molar heat capacities, $C_{p(co)} = 6.97$, $C_{p(co_2)} = 8.97$, $C_{p(o_2)} = 7.0$. **Ans.** −67762.5 cal

24. A gas is suspected to be Neon or Nitrogen. When a given sample of the gas at 25°C expanded adiabatically from 5 litres to 6 litres, the temperature came down to 4°C. What was the gas? **Ans.** Nitrogen

25. At 290°K, 15 cubic metre gas was compressed adiabatically from 1 atm to 6.5 atm. Calcualte final temperature and volume and also the work of compression in kilogram. ($\gamma = 1.2$).
Ans. $T = 396$°K., $V = 3.15\ m^3$, $W = -283700$ Kgm.

26. One litre of air ($\gamma = 1.4$) at 15°C expanded adiabatically until the volume was doubled. The original pressure was one atmosphere. What are the final pressure and temperature and what work have been done?

Ans. $T = -54.78°C$, $P = 0.38$ atm, $W = 61.36 \times 10^7$ ergs.

27. Show that

(*a*) $d \ln V = \alpha dT - \beta dP$

(*b*) $\left(\frac{\partial U}{\partial T}\right)_P = C_p - \alpha PV$

(*c*) $\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_v}{\alpha V} - P$

28. A rigid vessel is completely filled up with water at 25°C and then its temperature is raised to 35°C. If $\alpha = 2.07 \times 10^{-4}$ per degree and $\beta = 4.5 \times 10^{-6}$ per atm, show that the pressure developed will be 46 atm.

29. Ten cu. ft. of air at 14.7 lb per sq. in. and 15°C are compressed adiabatically to 3 cu. ft. Calculate final temp. and pressure. ($\gamma = 1.4$)

Ans. 194°C, 79.5 lb per sq. in.

30. One pound of air at 178.9°C expands adiabatically to three times its original volume when temp. falls to 15.6°C. The work done during expansion is 38410 ft.-lb. [$J = 1400$ ft.-lb (°C)]. Calcualte the two specific heats.

Ans. $C_v = 0.168$, $C_p = 0.2355$

31. If carbon monoxide at 270°F flows steadily in a tube at a velocity of 50 ft/sec at one point, what will be its temperature at another point where the velocity is 1200 ft/sec. The tube is horizontal and insulated. No shaft work is involved. Given $C_p = 7$ Btu/lb-mole (°F). Ans. 155°F

32. Estimate the work involved when 1 mole of an ideal gas at 25°C changes its pressure adiabatically and reversibly from 1.0 atm to 5.0 atm. [C_p (air) = 7 cal/mole]. Ans. -3.64 kj

33. The initial pressure and volume of an ideal gas are $p_1 = 75$ psia, $v_1 = 5$ ft^3. On changing, the pressure and volume are $p_2 = 25$ psia, $v_2 = 9.68$ ft^3. There is a decrease of 62 Btu in enthalpy during the change. Calculate the change in internal energy and C_p. [given $C_v = 0.75$ Btu/lb°R.]

[Hints : $\Delta H = \Delta U + (P_2V_2 - P_1V_1) = \Delta U + \frac{25 \times 9.68 \times 144 - 75 \times 5 \times 144}{778}$

whence $\Delta U = -37.4$ Btu

Again $C_p/C_v = \Delta H/\Delta U = -62/-37.4$]

34. One mole of an ideal gas at 27°C and 5 atm expands adiabatically under (*i*) reversible and (*ii*) irreversible conditions. Compute q, w, ΔU and ΔH in each case. (Given $C_v = 3/2.R$)

Solution : For reversible process :

$$q = 0$$

$$T_2 = T_1(P_2/P_1)^{R/Cp} = 300(\tfrac{1}{5})^{0\cdot 4} \approx 158°K$$

$$\Delta U = -w = C_v(T_2 - T_1) = \tfrac{3}{2} \times 8.314 \times (158 - 300) = -1.77 \text{ kj}$$

$$\Delta H = C_p(T_2-T_1) = (5/2)\times 8.314(158-300) = -\ 2.952 \text{ kj}$$

(*b*) For irreversible process :

$$W_{irr} = -\Delta U, \qquad \text{(since } q = 0)$$

$$= -P_2(V_2-V_1)$$

$$= P_2\left(\frac{RT_1}{P_1}-\frac{RT_2}{P_2}\right) = RT_1\frac{P_2}{P_1}-RT_2$$

But $-\Delta U = C_v(T_1-T_2) = RT_1\dfrac{P_2}{P_1}-RT_2$

or

$$T_2 = T_1 \,.\, \frac{C_v + \left(\dfrac{P_2}{P_1}\right) R}{C_p}$$

In the present case, $T_2 = 300\ \dfrac{3/2\,.\,R+\frac{1}{5}\,R}{5/2\ R} = 204°\text{K}$

$$q = 0;\ \Delta U = C_v(T_2-T_1) = \tfrac{3}{2}\times R\times(204-300) = -\ 1.197 \text{ kj}$$

$$w = -\Delta U;\ \Delta H = C_p(T_2-T_1) = \tfrac{5}{2}\times R\times(204-300) = -1.995 \text{ kj}$$

35. Helium behaves as a perfect monatomic gas and its internal energy at 2°K is zero. One litre of this gas is taken at 2°K and 0.025 atm.

(*i*) The gas is heated to 252°K at const. volume. Calculate the heat absorbed and the internal energy of the gas.

(*ii*) The gas is then expanded adiabatically until the temp. is 2°K. Find the work involved and the internal energy.

(*iii*) Next the gas is compressed isothermally till the original volume is reached. Calculate the work to be done.

Ans. (*i*) $q = \Delta U = 114.4$ cal. (*ii*) 480.48j (*iii*) −18.55j

36. Liquid air boils at −182°C. Assuming air ($C_p = \frac{7}{2}R$) to behave ideally, what should be the initial pressure of air at 0°C if its reversible adiabatic expansion to a pressure of 1 atm cools it to its boiling pt? **Ans.** 46.8 atm

37. An electron is accelerated through a potential difference of 200 volts. It then enters into a magnetic field of 20 oersteds perpendicular to its path. What is the radius of its circular path when in this field? **Ans.** 7.5 cm

38. Show that the rate of cooling of dry atmosphere with altitude will be

$$\frac{dT}{dh} = -\frac{\gamma-1}{\gamma}\cdot\frac{Mg}{R},$$ the process being adiabatic.

CHAPTER 3

THERMAL CHANGES IN CHEMICAL PROCESSES

All chemical reactions are accompanied with thermal changes. The reactions in which heat escapes from the system to the surroundings are called *exothermic*, while the chemical reactions in which heat is absorbed by the system from the surroundings are *endothermic*. The heat-change δq is not an exact differential, as its magnitude depends on the way the change is carried out.

When the chemical process is carried out at a constant pressure (which is quite usual), the heat-change is denoted by q_p. If the chemical process occurs at constant volume, the heat-change is denoted by q_v. Following the usual thermodynamic concept when heat escapes from the system, q is negative ; and when heat is absorbed by the system q is positive. The magnitudes of q_p and q_v may not be the same for the same chemical process. For example,

At 1000°K, $MgCO_3 = MgO + CO_2$; $q_p = 26000$ cal, $q_v = 24000$ cal

We know, $q_p = \triangle H$ and $q_v = \triangle U$. It is the usual custom to express the heat-changes on the right-hand side of the chemical equation in terms of $\triangle H$ and $\triangle U$. Thus,

Exothermic :
(*i*) $N_2 + 3H_2 = 2NH_3$; $\triangle H = -22.08$ Kcal
(*ii*) $HCl + NaOH = NaCl + H_2O$; $\triangle H = -13.40$ Kcal
(*iii*) $H_2 + Cl_2 = 2HCl$; $\triangle H = -22.1$ Kcal

Endothermic :
(*i*) $N_2 + O_2 = 2NO$; $\triangle H = +42.0$ Kcal
(*ii*) $2C + H_2 = C_2H_2$; $\triangle H = +54.2$ Kcal
(*iii*) $CO_2 = CO + \frac{1}{2}O_2$; $\triangle H = +67.6$ Kcal

The thermal-changes are usually expressed in units of calorie or joule.

3-1. q_p and q_v : We know,

$$q_p = \triangle H_p = \triangle U_p + P\triangle V$$

where $\triangle V$ is the change in volume of the system in the chemical process at constant pressure.

Also, $q_v = \triangle U_v$

Hence, $q_p - q_v = \triangle U_p - \triangle U_v + P\triangle V$

In systems of ideal gases, at constant temperature $\triangle U$ is independent of pressure or volume *i.e.* $\triangle U_p = \triangle U_v$. In other chemical reactions, these differ only very slightly and the difference between $\triangle U_p$ and $\triangle U_v$ is considered negligible compared to other heat effects. So,

$$q_p = q_v + P\triangle V \qquad \ldots (3.1)$$

In a gaseous reaction if n_2 and n_1 denote number of resultant and reactant molecules, then $P\triangle V = P(n_2 - n_1)\frac{RT}{P} = \triangle nRT$

$$\therefore q_p = q_v + \triangle nRT \qquad \ldots (3.2)$$

In computing $\triangle n$ of a reaction only the gaseous substances involved in the chemical process are to be considered ; the liquid or solid participants are to be ignored.

Example : (1) For the decomposition of $MgCO_3$, at 1000°K and 1 atm.

$$MgCO_3 = MgO + CO_2 ; \qquad q_p = 26000 \text{ cal}$$

Find the heat-change at constant volume.

Here $\triangle n = 1$, since MgO and $MgCO_3$ are solids and their volumes are negligible for our purpose.

$$\therefore q_v = q_p - \triangle nRT = 26000 - (1)\ (2)\ (1000) = 24000 \text{ cal}$$

Example : (2) The heat of combustion of liquid toluene to carbon dioxide and liquid water at const. volume is −928.8 Kcal at 500°K. Find q_p.

$$\underset{\text{liq}}{C_7H_8} + \underset{\text{gas}}{9O_2} = \underset{\text{gas}}{7CO_2} + \underset{\text{liq}}{4H_2O}$$

Here $\triangle n = 7 - 9 = -2$

$$\therefore q_p = q_v + \triangle nRT = -928.8 + (-2)\ (2\times10^{-3})\ (500) \text{ Kcal}$$
$$= -930.8 \text{ Kcal}$$

The heat-changes in chemical reactions also depend upon the physical state of the reactants and resultants. To indicate the physical states; gas, liquid and solid states are represented by *g*, *l* and *s* on the side of their formulae. For instance ;

$$2C_6H_6(l) + 15O_2(g) = 12CO_2(g) + 6H_2O(l) ; \qquad \triangle H = -781 \text{ kcal}$$
$$2C_6H_6(g) + 15O_2(g) = 12CO_2(g) + 6H_2O(l) ; \qquad \triangle H = -776$$
$$2C_6H_6(g) + 15O_2(g) = 12CO_2(g) + 6H_2O(g) ; \qquad \triangle H = -718$$

In the same way, the heats of burning of diamond and graphite to CO_2 are different. When the reactions occur in solution, the heats of reaction depend to some extent on the conc. of the solutions. In very dilute solutions, the heats of reaction attain a constant value.

Such solutions will not undergo any heat-change on further dilution. To express such a state of dilution, the symbol (*aq*) is often written on the side of the component concerned for aqueous systems.

$$H_2SO_4\ (aq) + 2NaOH\ (aq) = Na_2SO_4\ (aq) + 2H_2O; \quad \triangle H = -27.2 \text{ kcal}$$

3.2. The laws of thermochemistry

The thermal changes in chemical processes are governed by two general principles, both of which are, of course, corollaries of the First Law.

A. Law of Lavoisier and Laplace. This law states that *the heat-change accompanying a chemical process in one direction is equal in magnitude but opposite in sign, to that accompanying the same reaction in the reverse direction.* That is, heat evolved when water is formed from hydrogen and oxygen is exactly equal to the heat absorbed in the decomposition of water into the elements.

$$H_2(g) + \tfrac{1}{2}O_2(g) = H_2O\,(l); \qquad \triangle H = -68300 \text{ cal}$$
$$H_2O\,(l) = H_2(g) + \tfrac{1}{2}O_2(g); \qquad \triangle H = +68300 \text{ cal}$$

It is obvious from the first Law. Suppose two reactants A and B change first into C and D with heat evolution q_1. Subsequently C and D react to produce back A and B with heat absorbed q_2. It is a complete cycle and the enthalpy (H) and internal energy (U) of A and B will attain their initial values.

$$\therefore\ \Sigma\triangle H = 0, \quad \text{or} \quad q_1 + q_2 = 0$$

Hence, $q_1 = -q_2$

i.e. the heat-changes in the two opposite directions would be equal in magnitude but opposite in sign.

B. Hess's Law of Constant Heat Summation. This law states that *for a given chemical process, the net heat-change* (q_p or q_v) *will be the same whether the process occurs in one or in several stages.*

To illustrate, carbon and oxygen can give directly carbon dioxide, or these can first form carbon monoxide which may then be oxidised to carbon dioxide. The net heat-changes in either case will be the same.

(*a*) $C + O_2 = CO_2; \qquad q_P = -94.05$ Kcal

(*b*) $C + \tfrac{1}{2}O_2 = CO; \qquad q'_P = -26.42$ Kcal

$CO + \tfrac{1}{2}O_2 = CO_2; \qquad q''_P = -67.63$ Kcal

$C + O_2 = CO_2$ It is seen, $q_P = q'_P + q''_P$

In accordance with the First Law, if the initial and final states be fixed, the change in the heat-content or energy-content of a system *i.e.*, $\triangle H_p$ and $\triangle U_v$ would be independent of the path. Hence q_p and q_v will be independent of the path, *i.e.*, heat-change of a reaction will be the same whether the reaction takes place in a single step or in several steps.

One singular advantage of this principle is that we can add or subtract the heat-changes in the process, as we have seen in the example of carbon dioxide formation just now. In other words, the thermochemical equations may be treated algebraically. Some examples are given below:

Example : (3) The heats of oxidation of magnesium and iron are given :

(*a*) $Mg + \frac{1}{2}O_2 = MgO$; $\triangle H = -145700$ cal

(*b*) $2Fe + \frac{3}{2}O_2 = Fe_2O_3$; $\triangle H = -193500$ cal

Calculate the heat produced in the reaction : $3Mg + Fe_2O_3 = 3MgO + 2Fe$

Multiplying (*a*) by 3,

(*c*) $3Mg + \frac{3}{2}O_2 = 3MgO$; $\triangle H = -3\times145700$ cal

and reversing (*b*),

(*d*) $Fe_2O_3 = 2Fe + \frac{3}{2}O_2$; $\triangle H = +193500$ cal

Adding (*c*) and (*d*), $3Mg + Fe_2O_3 = 3MgO + 2Fe$; $\triangle H = -243600$ cal

Example : (4) 52.5 kcal and 172.5 kcal heats are evolved when lead is oxidised to litharge (PbO) and red lead (Pb_3O_4) respectively. What would be the thermal-change in oxidising litharge to red lead?

(*a*) $Pb + \frac{1}{2}O_2 = PbO$; $\triangle H = -52.5$ Kcal

(*b*) $3Pb + 2O_2 = Pb_3O_4$; $\triangle H = -172.5$ Kcal

From (a), (c) $3PbO = 3Pb + \frac{3}{2}O_2$; $\triangle H = +52.5\times3 = 157.5$ Kcal

Adding (b) and (c), $3PbO + \frac{1}{2}O_2 = Pb_3O_4$; $\triangle H = -172.5+157.5$
$= -15$ Kcal

Example : (5) The heats produced in the oxidation of cane sugar, carbon and hydrogen are given as

(*a*) $C_{12}H_{22}O_{11} + 12O_2(g) = 12CO_2(g) + 11H_2O(l)$; $\triangle H = -1350$ Kcal

(*b*) $C + O_2(g) = CO_2(g)$; $\triangle H = -94.05$ Kcal

(*c*) $H_2 + \frac{1}{2}O_2 = H_2O(l)$; $\triangle H = -68.3$ Kcal

Calculate the heat produced if the canesugar were produced directly from the elements.

We can rewrite (*a*) as

(*d*) $12CO_2(g) + 11H_2O(l) = C_{12}H_{22}O_{11} + 12O_2$; $\triangle H = +1350$ Kcal

Multiply (*b*) by 12 and (*c*) by 11 and add (*d*),

$12C + 11H_2 + \frac{11}{2}O_2 = C_{12}H_{22}O_{11}$; $\triangle H = 12(-94.05) + 11(-68.3)$
$+ 1350$ Kcal $= -529.9$ Kcal

Hence, by applying Hess's law we can compute the heat of a reaction in the formation of a compound though the elements would not directly combine to produce the compound.

These examples clearly illustrate the utility of the law of heat summation.

The heat of reaction at constant pressure, q_p, is really the enthalpy-change of the process and obviously it is the difference between the enthalpies of products and reactants.

$$q_p = \Delta H = H_{\text{products}} - H_{\text{reactants}} \quad \ldots (3.3)$$

The heat-changes involved in different transformations have been given different names depending upon the nature of the processes, such as heat of formation, heat of combustion, heat of dilution, etc. Below are appended the meanings of some commonly used terms:

3.3. Heat of formation

It is defined as the amount of heat-change that occurs when a gm-molecule of the substance is formed from the constituent elements. In the production of a mole of water from hydrogen and oxygen 68.3 kilo-calories of heat are evolved. Hence, the heat of formation of water is —68.3 Kcal.

Symbolically, $H_2 + \frac{1}{2}O_2 = H_2O$; $\Delta H_f = -68.3$ Kcal

Thus '—94050 calories is the heat of formation of carbon dioxide' means that when, 1 gm-mol of CO_2 is obtained from carbon and oxygen, the heat evolved would be 94050 calories.

If heat is evolved during the formation of the compound from its elements, the compound is an *exothermic* one. On the other hand, if heat is absorbed in the formation of a compound, as in nitric oxide, the compound is called, *endothermic*. Examples :

(*a*) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) = NH_3(g)$; $\Delta H_f{}^0 = -11030$ cal

(*b*) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(g)$; $\Delta H_f{}^0 = -57790$ cal

(*c*) $H_2(g) + I_2(s) = 2HI(g)$; $\Delta H_f{}^0 = +11900$ cal

(*d*) $C(s) + 2S(s) = CS_2(g)$; $\Delta H_f{}^0 = +25400$ cal

The subscript 'f' denotes formation of the compound from the elements.

Now ΔH is the difference of enthalpies of products and reactants.

Suppose the elements A and B unite to form a compound C.

$$A + B \rightarrow C$$

The heat of formation of *C*, from equation (3.3),

$$\triangle H_{f(c)} = H_C - H_A - H_B$$

The enthalpy of a substance depends upon pressure and temperature. The standard temperature for thermo-chemical measurements has been chosen as 298°K and pressure 1 atm. The standard enthalpy is H° ; the superscript 'o' indicating standard state. We can then write,

$$\triangle H^\circ_{f(c)} = H^\circ_C - H^\circ_A - H^\circ_B$$

In order to measure $\triangle H$, it is necessary to assign some definite value for the enthalpies of reactants and products. It has been decided to assign the value *zero* for enthalpy of every element at 298°K and 1 atm. When an element occurs in different modifications, the most stable allotrope is given the value zero. Thus, at 1 atm and 298°K, carbon (graphite), sulphur (rhombic), nitrogen, oxygen, magnesium, copper, . . . all have zero enthalpy.

Hence, $\triangle H^\circ_{f(c)} = H^\circ_C - H^\circ_A - H^\circ_B = H^\circ_C$;

$(\because\ H^\circ_A = H^\circ_B = 0)$

$$\therefore \triangle H^\circ_{f(c)} = H^\circ_C \qquad \ldots (3.4)$$

That is, *the standard enthalpy of a compound = its standard heat of formation.*

Then, for any reaction, $A + B \rightarrow C + D$,

$$\triangle H^\circ_{\text{reaction}} = H^\circ_C + H^\circ_D - H^\circ_A - H^\circ_B$$

$$= \triangle H^\circ_{f(c)} + \triangle H^\circ_{f(D)} - \triangle H^\circ_{f(A)} - \triangle H^\circ_{f(B)}$$

$$\text{or } \triangle H^\circ_{\text{reaction}} = \Sigma \triangle H^\circ_{f(\text{products})} - \Sigma \triangle H^\circ_{f(\text{reactants})} \qquad \ldots (3.5)$$

The heat of a reaction can be computed from the heats of formation of the participants.

Example : (6) When liquid benzene burns in oxygen producing $CO_2(g)$ and liquid water, the heat evolved is −781 Kcal per mole. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are −94.05 and −68.3 Kcal respectively. Calculate the heat of formation of liquid benzene.

Given $2C_6H_6(l) + 15O_2(g) = 12CO_2(g) + 6H_2O(l)$; $\triangle H = -2\times781$ Kcal

$\triangle H^\circ_f \rightarrow 2x \quad 0 \quad (-12\times94.05) \quad (-6\times68.3)$

where x is the heat of formation of $C_6H_6(l)$.

$\therefore \quad \triangle H_{\text{reaction}} = \triangle H_{f(CO_2)} + \triangle H_{f(H_2O)} - 2x$

or $\quad -2\times781 = -12\times94.05 - 6\times68.3 - 2x$

whence $\quad x = 12.3$ Kcal.

The result is somewhat higher than the standard value, as the computation involves the difference of two large heat-effects.

This illustrates that heat of formation can be evaluated from some heats of combustion.

Example : (7) The heats of formation of carbon dioxide from diamond and graphite are −94500 cal and −94050 cal respectively. Find out the enthalpy-change in the transition of diamond to graphite.

$$C_{dia} + O_2 = CO_2; \qquad \Delta H_1^0 = -94500 \text{ cal}$$
$$C_{gra} + O_2 = CO_2; \qquad \Delta H_2^0 = -94050 \text{ cal}$$
$$\text{Subtracting} \quad C_{dia} = C_{gra}; \qquad \Delta H^0 = -450 \text{ cal.}$$

Thus, the enthalpy-change of transition can be evaluated from heats of formation.

Example : (8) For the reaction,

$$CO + NO = \tfrac{1}{2}N_2 + CO_2; \qquad \Delta H^0 = -374 \text{ kJ}$$

Find out the heat of formation of CO, if $\Delta H^0_{f(NO)} = +90.2$ kJ and $\Delta H^0_{f(CO_2)} = -394$ kJ

$$\text{Now,} \quad \Delta H^\circ = \tfrac{1}{2}\Delta H^\circ_{f(N_2)} + \Delta H^\circ_{f(CO_2)} - \Delta H^\circ_{f(CO)} - \Delta H^\circ_{f(NO)}$$
$$\text{or} \quad -374 = \tfrac{1}{2}\times 0 + (-394) - (90.2) - \Delta H^\circ_{f(CO)}$$
$$\text{or} \quad \Delta H^\circ_{f(CO)} = -110.2 \text{ kJ}$$

A few standard heats of formation have been assembled in the Table here.

TABLE : STANDARD HEATS OF FORMATION AT 25°C IN KCAL/MOLE

Substance	ΔH°_f	*Substance*	ΔH°_f
H_2O (g)	− 57.79	Na_2O (s)	− 99.4
H_2O (l)	− 68.32	CuO (s)	− 37.10
HCl (g)	− 22.06	PbO (s)	− 52.5
HBr (g)	− 6.83	ZnO (s)	− 83.17
HI (g)	+ 6.33	Al_2O_3 (s)	−399.09
N_2O (g)	+ 19.49	CaO (s)	−151.90
NO (g)	+ 21.6	NaCl (s)	− 98.23
CO (g)	− 26.42	KCl (s)	−104.17
CO_2 (g)	− 94.05	CH_4 (g)	− 17.89
SO_2 (g)	− 70.9	C_2H_6 (g)	− 20.24
NH_3 (g)	− 11.04	C_2H_4 (g)	+ 12.50
HNO_3 (l)	− 41.4	C_2H_2 (g)	+ 54.19
H_2S (g)	− 5.3	C_6H_6 (l)	+ 11.70
NaOH (s)	−102.00	CH_3OH (l)	− 57.02
KOH (s)	−102.00	C_2H_5OH (l)	− 66.36

3.4. Heat of Combustion

The heat-change accompanying the complete combustion of a gm-mole of the substance at a given temperature under normal pressure is called its *heat of combustion.*

In estimating heat of combustion, the substance must be allowed to be oxidised to its final state. In the case of organic compounds, complete combustion is regarded to have taken place when these are transformed finally into CO_2 and H_2O. A few data for heats of combustion are given below:

TABLE : HEATS OF COMBUSTION AT 25°C IN KCAL

Compounds	$\triangle H$	*Compounds*	$\triangle H$
Methane	– 212.8	Methanol (*l*)	– 173.6
Ethane	– 372.8	Ethanol (*l*)	– 326.7
Ethylene	– 337.2	Cane sugar (*s*)	–1349.0
Acetylene	– 310.6	Phenol (*s*)	– 732.0
Benzene (*l*)	– 780.9	Aniline {*l*)	– 812.0
Naphthalene (*s*)	–1228.2	Benzoic acid (*s*)	– 771.4

The heat of combustion is usually determined in a 'bomb-calorimeter' internally enamelled with platinum and capable of withstanding high pressure (Fig. 3*a*). It has a capacity of about 400 c.c. and is fitted with pressure-tight screw-cap. A weighed sample is placed in a cup inside and the bomb is filled with oxygen at 25–30 atm. The bomb is kept immersed in water in a calorimeter. When the system acquires a constant temp T_1, the reaction is initiated by passing a small electric current through the thin pt-wire dipped in the sample. The reaction produces a large amount of heat and the temperature-rise is accurately determined. In a separate control experiment, the products plus calorimeter are raised from $T_1°$ to $T_2°$ by electric heating, and the amount of electric energy used, Eit is measured in the usual way. Evidently this energy (Eit) is equivalent to the heat produced during combustion. Remembering that the reaction occurred at constant volume,

$$q_v = -Eit$$

The experimentally determined heats of combustion are quite useful in evaluation of heats of formation or heats of other reactions.

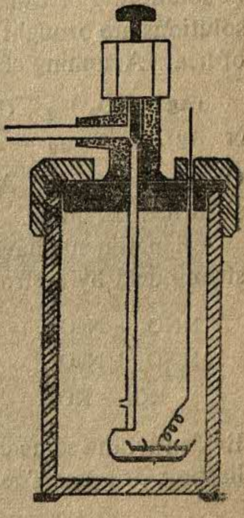


Fig. 3*a*
'Bomb calorimeter'

Example : (9) Calculate the heat of formation of ammonia. The heats of combustion of ammonia and hydrogen are −90.6 and −68.3 Kcal respectively.

Given (1) $2NH_3 + \frac{3}{2}O_2 = N_2 + 3H_2O$; $\Delta H = -2 \times 90.6 = -181.2$
(2) $H_2 + \frac{1}{2}O_2 = H_2O$; $\Delta H = -68.3$
or (3) $3H_2 + \frac{3}{2}O_2 = 3H_2O$; $\Delta H = -3 \times 68.3$

Subtracting (3) from (1) and re-arranging

$2NH_3 = N_2 + 3H_2$; $\Delta H = -181.2 + 3 \times 68.3 = +23.7$
i.e., (4) $N_2 + 3H_2 = 2NH_3$; $\Delta H = -23.7$
Hence, heat of formation of ammonia, $\Delta H_f = -11.8$ Kcal

Example : (10) The heat of combustion of ethyl alcohol is 325100 calories and that of acetic acid is 209500 calories. Calculate the heat evolved in the reaction, $C_2H_5OH + O_2 = CH_3COOH + H_2O$.

Given (1) $C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O$; $\Delta H = -325100$ cal
(2) $CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$; $\Delta H = -209500$ cal

Subtracting (2) from (1) ; $C_2H_5OH + O_2 = CH_3COOH + H_2O$; $\Delta H = -115600$ cal. The heat of reaction is thus obtained from heats of combustion.

3.5. Heat of neutralisation

There are also thermal changes when ionic reactions occur in solution. For example, when silver nitrate and sodium bromide solutions are brought together, solid AgBr is formed, with evolution of heat. Assuming complete dissociation for salts, we have,

$$(Ag^+ + NO_3^-)_{aq} + (Na^+ + Br^-)_{aq} = (Na^+ + NO_3^-)_{aq} + AgBr(s)$$

or $Ag^+_{aq} + Br^-_{aq} = AgBr(s)$; $\Delta H = -3.6$ Kcal

Obviously, if solid AgBr dissolves in water 3.6 Kcal heat will be absorbed per mole.

Experiments have shown that the heat of neutralisation of any strong acid by a strong alkali is practically the same, e.g.,

$HNO_3 + NaOH = NaNO_3 + H_2O$, $\Delta H = -13.7$ Kcal
$\frac{1}{2}H_2SO_4 + NaOH = \frac{1}{2}Na_2SO_4 + H_2O$, $\Delta H = -13.6$ Kcal
$HCl + KOH = KCl + H_2O$, $\Delta H = -13.4$ Kcal etc.

Evidently, the same chemical change is taking in every such neutralisation process. The reaction is

$$H^+ + NO^-_3 + Na^+ + OH^- = Na^+ + NO_3^- + H_2O$$

i.e.,

$$H^+ + OH^- = H_2O$$

Since the strong acids, alkalis and the salts are all completely dissociated in solution, neutralisation means formation of water from H^+ and OH^- ions and the heat of this neutralisation reaction is -13.4 Kcal approx.

When a weak acid or a weak base is neutralised the heat of reaction is observed to be much less. For example,

$$HBO_2 + NaOH \rightarrow NaBO_2 + H_2O; \quad \Delta H = -10.0 \text{ Kcal}$$

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O; \quad \Delta H = -12.3 \text{ Kcal}$$

Being weak, complete dissociation does not take place, the reactions occur as follows :

$$HBO_2 \rightarrow H^+ + BO_2^- ; \quad \Delta H_d = \text{? (heat of dissociation)}$$

$$H^+ + OH^- \rightarrow H_2O ; \quad \Delta H = -13.4 \text{ Kcal}$$

Adding, $HBO_2 + OH^- = H_2O + BO_2^- ; \quad \Delta H' = \Delta H_d + (-13.4)$

Experimentally $HBO_2 + OH^- = H_2O + BO_2^- ; \quad \Delta H' = -10.0$ Kcal

$\therefore \quad -10 = \Delta H_d - 13.4$, or $\Delta H_d = 3.4$ Kcal

It means 3.4 Kcal heat has been used up in dissociating HBO_2.

The heats of electrolytic reactions also enable us to obtain an idea of the relative enthalpies of the formation of ions in dilute aqueous solutions from the elements in their standard states.

We know, (*i*) $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l) ; \quad \Delta H = -68.3$ Kcal

(*ii*) $H_2O(l) = H^+_{aq} + OH^-_{aq} ; \quad \Delta H = +13.4$ Kcal

Adding (*iii*) $H_2(g) + \frac{1}{2}O_2(g) = H^+(aq) + OH^-(aq) ;$

$\Delta H = -54.9$ Kcal

The enthalpy of elements is zero, hence, the heat of reaction obtained in (*iii*) is the sum of the enthalpies of formation of two ions. Heat of formation of an individual ion is not obtained. But difference of heats of formation of two ions can be obtained. Thus,

$$\tfrac{1}{2}H_2(g) + \tfrac{1}{2}Br_2(g) = H^+(aq) + Br^-(aq), \quad \Delta H = -28.90 \text{ Kcal}$$

$$Ag(s) + \tfrac{1}{2}Br_2(g) = Ag^+(aq) + Br^-(aq), \quad \Delta H = -3.6 \text{ Kcal}$$

Subtracting, $\Delta H_f(Ag^+)_{aq} - \Delta H_f(H^+)_{aq} = -3.6-(-28.9) = 25.3$ Kcal

In this way, difference in ΔH_f of many pairs of ions can be obtained. To get a definite value for the enthalpy of formation of an ion, it has been accepted, by convention, to put zero enthalpy for $H^+(aq)$. So, we see,

$\Delta H_f(OH^-)_{aq} = -54.9$ Kcal, $\quad \Delta H_f(Ag^+)_{aq} = +25.3$ Kcal

A Table of the enthalpies of different ions in aqueous solution is given here.

TABLE: ENTHALPIES OF FORMATION OF IONS IN DILUTE AQUEOUS SOLUTION (298°K) IN KCAL/MOLE

Ion.	ΔH_f	Ion.	ΔH_f	Ion.	ΔH_f	Ion.	ΔH_f
H^+	0	Ag^+	+25.31	OH^-	−54.9	I^-	− 13.4
Na^+	−57.3	Zn^{++}	−36.43	Cl^-	−40.0	NO_3^-	− 49.4
K^+	−60.04	Cu^{++}	+15.39	Br^-	−28.9	SO_4^{--}	−217.0

These values enable us to evaluate the heat-changes of ionic reactions in solution. For the reaction in the Daniell cell.

$$\begin{array}{lccccc} & Zn(s) & + Cu^{++} & = & Cu(s) & + Zn^{++} \\ \Delta H_f \rightarrow & 0 & \Delta H_f(Cu^{++}) & & 0 & \Delta H_f(Zn^{++}) \end{array}$$

$$\therefore \quad \Delta H_{\text{reaction}} = 0 + (-36.43) - 0 - (15.39); \qquad \text{(from the table)}$$
$$= -51.82 \text{ Kcal}$$

3.6. Heats of solution and dilution

The amount of heat released or absorbed when a solute dissolves in a solvent is called the *heat of solution*. For quantitative expression, the heat-change associated with the dissolution of 1 gm mole of solute is called the *integral heat of solution* (ΔH). But this thermal change also depends upon the number of moles of the solvent (n_1). Thus, if n_2 represents the moles of solute, then

$$\Delta H = f(n_1, n_2)$$

$$\text{or} \quad d(\Delta H) = \left(\frac{\partial(\Delta H)}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial(\Delta H)}{\partial n_2}\right)_{n_1} dn_2$$

Putting $\overline{\Delta H_1}$ for $\left(\frac{\partial(\Delta H)}{\partial n_1}\right)_{n_2}$ and $\overline{\Delta H_2}$ for $\left(\frac{\partial(\Delta H)}{\partial n_2}\right)_{n_1}$, we have

$$d(\Delta H) = \overline{\Delta H_1} dn_1 + \overline{\Delta H_2} dn_2 \qquad \ldots (3.6)$$

$\overline{\Delta H_1}$ means the change in the heat of solution when 1 mole of solvent is added to a quantity of solution which is very large and the addition of solvent scarcely affects the concentration. Likewise, $\overline{\Delta H_2}$ represents the heat of solution when 1 mole of solute is added under the same conditions. $\overline{\Delta H_2}$ is called *differential heat of solution*. It is also known as 'partial molal heat of solution'.

In the table below are shown the changes in heat effects per mole of solute when dissolved in different quantities of solvent.

TABLE: INTEGRAL HEATS OF SOLUTION (298°K) IN CALORIES PER MOLE OF SOLUTE (SOLVENT WATER)

Solute : KCl		Solute : H_2SO_4	
Moles $H_2O(n_1)$	$\triangle H$ (cal)	Moles H_2O (n_1)	$\triangle H$ (cal)
0	0	0.10	− 900
12	+3786	0.25	− 1970
50	+4276	0.67	− 4900
100	+4391	1.00	− 6750
150	+4425	1.50	− 8630
200	+4449	4.00	−13000
∞	+4450	∞	−20000

Evidently one mole of KCl dissolved in 12 moles of water and in 200 moles of water will cause different heat-change. If $\triangle H$ is plotted against n_1, the graph ultimately becomes parallel to the conc^n-axis at high values of n_1, *i.e.* when the solution becomes very dilute, the heat-change attains a constant value, called the heat of solution at infinite dilution (Fig. 3*b*).

Since the heat of solution varies with concentration the addition of a quantity of solvent to a given solution of fairly high concentration would involve a thermal change. The net heat-change associated with the dilution of a solution containing 1 mole of solute from a concentration C_1 to a concentration C_2 is called the *integral heat of dilution*. These integral heats of dilution are evidently the differences of the heats of solution at the corresponding concentrations.

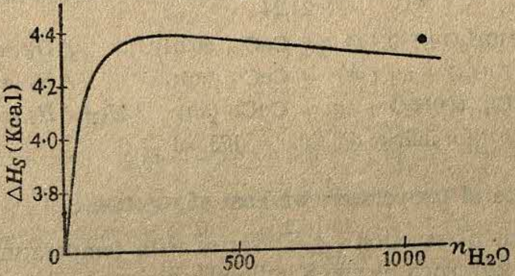


Fig. 3*b*. Variation of Heat of solution of KCl with dilution

Thus $\qquad KCl\ (s) + 50H_2O = KCl(50H_2O) - 4276$ cal

and $\qquad KCl\ (s) + 100H_2O = KCl(100H_2O) - 4391$ cal

By subtraction, $KCl\ (50H_2O) + 50H_2O = KCl\ (100H_2O) - 115$ cal
i.e., in diluting $KCl\ (50H_2O)$ to half its concentration another 115 calories of heat would be absorbed.

$\triangle H_1$ (eqn. 3.5) is the rate of change of heat of dilution with concentration and it varies with concentration. $\triangle H_1$ is hence called the 'differential heat of dilution' or partial molal heat of dilution.

Example : (11) A solution of composition $CuCl_2 + 10H_2O$ is diluted with x moles of water, the heat disengaged is given by $Q_V = \dfrac{x \times 5023}{x + 21.24}$. The heat of solution of $CuCl_2$ in 600 moles of water is 11080 calories. Find out the heat of solution of anhydrous $CuCl_2$ in 10 moles of water. What heat would be evolved if a solution $CuCl_2 + 600H_2O$ be infinitely diluted?

We have (*a*) $CuCl_2,\ 10H_2O + 590H_2O = CuCl_2,\ 600H_2O;$

$$\triangle H_0 = -Q_V = -4850 \text{ cal}$$

$$\therefore \quad Q_V = \frac{x \times 5023}{x + 21.24} = \frac{590 \times 5023}{590 + 21.24} = 4850 \text{ cal}$$

But (*b*) $CuCl_2 + 600H_2O = CuCl_2,\ 600H_2O;$ $\triangle H_1 = -11080$ cal

Subtracting, $CuCl_2 + 10H_2O = CuCl_2,\ 10H_2O;$ $\triangle H = -11080+4850$

$= -6230$ cal

$\therefore$ Heat of solution of $CuCl_2$ in 10 moles of water $= -6230$ cal

Again, if $x = \infty,\ Q_\infty = \dfrac{x \times 5023}{x + 21.24} = \dfrac{x \times 5023}{x} = 5023$ cal

Then $CuCl_2,\ 10H_2O+590H_2O = CuCl_2,\ 600H_2O;$ $\triangle H_0 = -4850$ cal

and $CuCl_2,\ 10H_2O + aq\ (\infty) = CuCl_2\ (aq);$ $\triangle H_2 = -5023$ cal

$\therefore$ $CuCl_2,\ 600H_2O + aq = CuCl_2\ (aq);$ $\triangle H_2 - \triangle H_0 = -\ 173$ cal

i.e., Evolved heat for infinite dilution = 173 cal

3-7. Influence of temperature on heat of reaction

The heat of reaction ($\triangle H$) varies with temperature and this variation is governed by the Kirchhoff's equation (Sec. 2-9.)

$$\left[\frac{\partial(\triangle H)}{\partial T}\right]_P = \triangle C_p = \Sigma C_{p\,\text{products}} - \Sigma C_{p\,\text{reactants}}$$

Integrating $\triangle H_{T_2} - \triangle H_{T_1}$

$$= \int_{T_1}^{T_2} \Sigma C_{p\,\text{products}}\, dT - \int_{T_1}^{T_2} \Sigma C_{p\,\text{reactants}}\, dT \quad \ldots (3.7)$$

Hence a knowledge of the heat of reaction at T_1 and the heat capacities of the reactants and resultants would enable the evaluation of the heat of reaction at some other temperature T_2. This has been illustrated in examples (10, 11, 12) in sec. 2-9.

3.8. Influence of pressure on the heat of reaction

It would be easier to follow the effect of pressure on heat of reactions by anticipating a thermodynamic relation for the rate of change of enthalpy with pressure, namely,

$$\left(\frac{dH}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

Consequently, $$\left[\frac{\partial(\Delta H)}{\partial P}\right]_T = \Delta V - T\left[\frac{\partial(\Delta V)}{\partial T}\right]_P \qquad \ldots (3.8)$$

where ΔH = heat of reaction ; and ΔV = volume-change of the reaction at constant pressure P.

Now, coefficient of expansion : $\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$; or $\alpha V = \left(\frac{\partial V}{\partial T}\right)_P$

Hence $$\alpha_2 V_2 - \alpha_1 V_1 = \left[\frac{\partial(V_2 - V_1)}{\partial T}\right]_P = \left[\frac{\partial(\Delta V)}{\partial T}\right]_P$$

Where suffixes 1, 2 are for reactants and products.

$$\therefore \qquad \Delta(\alpha V) = \left(\frac{\partial(\Delta V)}{\partial T}\right)_P$$

$\therefore$ Integrating eqn. 3.8. , at a given temperature T,

$$\Delta H_{P_2} - \Delta H_{P_1} = \int_{P_1}^{P_2} [\,\Delta V - T\Delta(\alpha V)]\, dP \qquad \ldots (3.9)$$

This is the required relation.

For reactions involving ideal gases only, $\left[\frac{\partial(\Delta H)}{\partial P}\right]_T$ is zero, as enthalpies of ideal gases are independent of pressure. The equation (3.9) can be utilised only when necessary equations of state are known.

3.9. Maximum Flame Temperature

When gaseous fuels burn producing flames, large amounts of heat are evolved. If the transfer of this heat to the surroundings or dissipation is small and ignored, the process may be regarded as an adiabatic one at constant pressure. The entire heat produced from the chemical reaction is utilised instantly in raising the temperature of the gaseous products in the flame-zone. The initial temperature of the fuel gas and the oxidant (often air) is known. If we also know the heat of reaction as well as the composition and heat-capacities of the resultant gases, it would be quite simple to find out the high temperature to which these gases would be raised in the flame. Since no heat has been allowed to dissipate, the calculated temperature would be the maximum for the flame. It is necessary to remember, that not only the gaseous products of reaction would be heated but any inert gas (say nitrogen) present in the system would also be heated. This may be illustrated with an example.

Example : (12) What maximum temperature can be reached by the complete combustion of methane with 20% excess air? The initial temperature of air and methane entering the burner is 25°C. Assume the standard heat of combustion of methane as −200 Kcal and air to contain $O_2 : N_2 = 1 : 4$ ratio.

$$CH_4 + 2O_2 = CO_2 + 2H_2O \,; \qquad \Delta H = -200.000 \text{ cal}$$

Air introduced (20% excess) contained 2.4 mole O_2, 9.6 moles N_2. The composition of the product would be CO_2 1 mole, $H_2O(g)$ 2 moles, O_2 0.4 moles, N_2 9.6 moles.

Since the heat of reaction is wholly used in raising the temp. of the products, say to t°C, then

$$[\,2C_{p(H_2O)} + C_{p(CO_2)} + 0.4\;C_{p(O_2)} + 9.6\;C_{p(N_2)}\,]\,(t-25) = -200.000$$

To solve, it would be convenient if we make a trial with an estimated temperature, say 2000°C. Substituting the C_p-values at 2000°C from the standard C_p vs t curves for these gases (Fig 3*c*), we have,

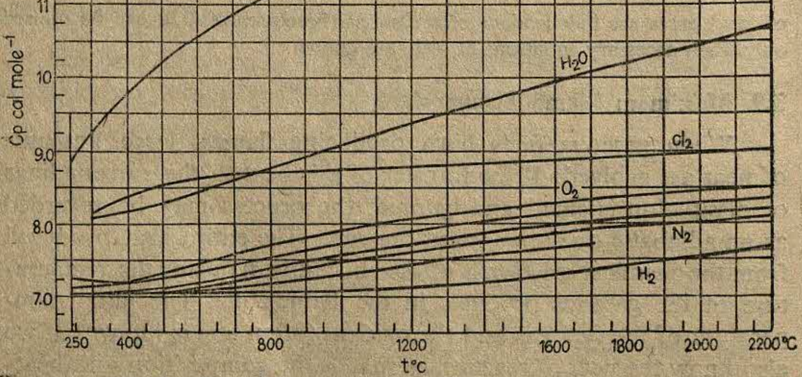


Fig 3*c*. Plot of heat capacities (C_p) versus temperature

$$[2 \times 10.4 + 1 \times 13.1 + 0.4 \times 8.4 + 9.6 \times 8.0]\ (t - 25) = 200.000$$

$$\text{whence} \quad t = 1780°\text{C}$$

Evidently t will have a magnitude less than 2000°C.

In the next trial let us assume the temp. to be 1800°C, then from the graph,

$$[2 \times 10.3 + 1 \times 12.95 + 0.4 \times 8.3 + 9.6 \times 8.0]\ (t - 25) = 200.000$$

$$\text{whence} \quad t = 1805°\text{C}$$

∴ The maximum temp. of the flame would be approximatey 1800°C.

Example : (13) Air contains oxygen and nitrogen in the ratio 1 : 4. A gm-mole of H_2 at 25°C mixed with air just sufficient for its combustion is exploded in a constant-volume bomb. What is the temperature attained? Given heat of combustion of hydrogen, $\Delta H_{298} = -57.8$ Kcal. and $C_v(H_2O, g) = 5.7$ cal/mole, $C_v(N_2, g) = 4.98$ cal/mole.

Before reaction, gas mixture consists of $H_2 = 1$ mole, $O_2 = \frac{1}{2}$ mole and hence $N_2 = 2$ moles.

$$\text{Now,} \quad H_2(g) + \tfrac{1}{2}O_2(g) = H_2O(g), \qquad \Delta n = -\tfrac{1}{2}$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\therefore\ -57800 = \Delta U - \tfrac{1}{2} \times 2 \times 298, \text{ or} \quad \Delta U = -57502 \text{ cal}$$

This energy is supposed to have heated the product one mole of $H_2O(g)$ and 2 moles of N_2 (unreacted).

$$\therefore\ 57502 = \int_{298}^{T} 5.7\, dT + \int_{298}^{T} 2 \times 4.98\, dT$$

$$= [5.7 + 2 \times 4.98]\ [T - 298]$$

$$\text{or} \qquad T \approx 3900°\text{K}.$$

The answer is approximate, for, the change is reversible and hence unreacted H_2-O_2 will remain to some extent. Some heat will certainly radiate out. And C_v values are not constant throughout the temp-range.

3-10. Bond Energy and Bond Dissociation Energy

The heat of reaction of all chemical changes can be evaluated provided the heats of formation of hundreds of thousands of compounds are known (eqn 3-5), which is a formidable task. An alternative technique to ascertain the heats of reaction can be profitably employed by using what is known as the 'bond energy'. But for this purpose, it would be necessary to consider the structure of molecules, thereby overstepping the strict boundaries of classical thermodynamics.

The amount of energy required to separate an atom by breaking its bond or link with another atom in a given compound is called the '*bond-dissociation energy*' (q_D) of that bond. This bond-dissociation energy depends on the nature of the atoms united by the bond as well as the nature of the molecule as a whole, *i.e.* environment of the bond. To wit, the dissociation energy of separating a H-atom from water by breaking one O–H bond is 118 kcal (or 494 kj) per mole.

$$H_2O \rightarrow H + OH\ ; \qquad q_D = +118 \text{ Kcal}$$

But when the second H-atom is separated from the residual O–H group, the dissociation energy is less ;

$$O - H \rightarrow H + O\ ; \qquad q'_D = +103 \text{ Kcal}$$

On the other hand, the average value of the dissociation energies of a given bond in a series of different dissociating species is called '*bond-energy*' (q_B) of that bond.

So, the bond-energy of the O – H bond will be the average of q_D and q'_D obtained above.

$$\therefore \text{ OH bond-energy} = \frac{q_D + q'_D}{2} = \frac{118 + 103}{2}$$

$$= 110.5 \text{ kcal/mole}$$

Experimentally, $H_2O(g) = H_2(g) + \frac{1}{2}O_2(g)$;

$$\Delta H = 110 \text{ kcal/mole}$$

Let us take another example as that of methane. The successive separation of a H-atom from methane per mole in the gaseous state are as follows :

	dissociation energy mol^{-1}
(*i*) $CH_4 \rightarrow CH_3 + H$;	$q_1 = 435$ kj
(*ii*) $CH_3 \rightarrow CH_2 + H$;	$q_2 = 444$ kj
(*iii*) $CH_2 \rightarrow CH + H$;	$q_3 = 444$ kj
(*iv*) $CH \rightarrow C + H$;	$q_4 = 339$ kj

The bond-energy (C–H) $= \frac{1}{4}\Sigma q_D = \frac{1}{4} \times 1662$

$= 415.5$ kj/mole (99kcal/mole)

The determination of bond-dissociation energy is often difficult. Some accurate values have been estimated from mass spectrometry and ultraviolet spectroscopy.

The ΔH-value for the complete breakdown of methane into carbon and 4 hydrogen atoms has been computed in the following way:

	ΔH (Kcal)
(*i*) $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$,	-212.8
(*ii*) $CO_2(g) = C_{gr} + O_2(g)$	$+94.05$
(*iii*) $2H_2O(l) = 2H_2(g) + O_2(g)$	$+136.64$
(*iv*) $2H_2(g) = 4H(g)$	$+208.38$
(*v*) $C_{gr} = C(g)$	$+171.29$
$CH_4(g) = C_{gr} + 4H(g)$	$\Delta H = 397.6$ kcal

$\therefore$ Bond-energy (C$-$H) $= \frac{1}{4} \times 397.6 = 99.4$ Kcal/mole

This conforms to the calculated value given above.

Some of the bond-energy values are given in the table here.

Bond energy at 298°K per mole

Bond	q_B (Kcal/mole)	Bond	q_B (Kcal/mole)
H $-$ H	104.2	C $-$ H	98.7
C $-$ C	82.6	N $-$ H	93.4
C $=$ C	145.8	O $-$ H	110.6
C $\equiv$ C	199.6	F $-$ H	135
O $-$ O	35.0	Cl $-$ H	103.1
O $=$ O	119.1	S $-$ H	83
N $-$ N	39.0	Br $-$ H	87.4
N $\equiv$ N	225.8	C $-$ Cl	81
F $-$ F	37.0	N $-$ Cl	46
Cl $-$ Cl	57.87	O $-$ Cl	52
Br $-$ Br	46.08	P $-$ Cl	78
I $-$ I	36.0	I $-$ H	71.4
C $-$ O	85.5	C $-$ N	72.8
C $=$ O	178	C $\equiv$ N	212.6
C $=$ S	128	S $-$ S	54

Heat of atomisation

The *standard state* of an element is the state in which the element exists at 25°C and one atmosphere. The quantity of heat required to produce one mole of atoms in the gaseous atomic state from the element in the standard state is called the *heat of atomisation* of the element. The heats of atomisation of the elements are determined from spectroscopic measurements and some thermal data.

The most important and yet most difficult and uncertain is the determination of the heat of atomisation of carbon. The following procedure was used.

Cal

(1) $C(gr) + O_2(g) \rightarrow CO_2(g)$; $\Delta H_1 = -94200$

(2) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$; $\Delta H_2 = -67700$

(3) $\frac{1}{2}O_2(g) \rightarrow O(g)$; $\Delta H_3 = +58700$

(4) $CO(g) \rightarrow C(g) + O(g)$; $\Delta H_4 = +256500$

(5) $C(gr) \rightarrow C(g)$; ΔH = ? (heat of atomisation)

The first two values are obtained calorimetrically and (3) and (4) are determined spectroscopically. Obviously, the heat of atomisation of graphite,

$$\Delta H = \Delta H_1 - \Delta H_2 - \Delta H_3 + \Delta H_4 = -94200 + 67700 - 58700 + 256500 = 171.3 \text{ Kcal}$$

A few accepted values of the heats of atomisation are given here.

TABLE : HEAT OF ATOMISATION IN KCAL

Element	*Atomisation*	*Heat of atomisation (Kcal)*
Carbon	$C(s, gr) \rightarrow C(g)$	170.9
Hydrogen	$\frac{1}{2}H_2(g) \rightarrow H(g)$	52.1
Oxygen	$\frac{1}{2}O_2(g) \rightarrow O(g)$	59.6
Nitrogen	$\frac{1}{2}N_2(g) \rightarrow N(g)$	113.0
Chlorine	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	28.9

Calculation of Bond-energy

The knowledge of the heats of formation of a substance and the heats of atomisation of the constituents enables us to evaluate the bond-energy.

I. C-H bond energy : The heat of formation of methane is − 17.9 Kcal.

(*a*) $C(s) + 2H_2(g) = CH_4$; $\Delta H_f = -17.9$

and we know

(*b*) $C(s) = C(g)$; $\Delta H = 170.9$

(*c*) $2H_2(g) = 4H(g)$; $\Delta H = 4 \times 52.1$

Rearranging (*a*), (*d*) $CH_4 = C\,(s) + 2H_2\,(g)$; $\Delta H = +17.9$

Adding (*b*), (*c*) and (*d*), $CH_4 = C\,(g) + 4H\,(g)$; $\Delta H = 17.9 + 170.9 + 4 \times 52.1 = 397.2$ Kcal

That is, the energy required for breaking four C-H bonds = 397.2 Kcal

$\therefore$ C-H bond-energy = $\frac{1}{4} \times 397.2 \approx 99$ Kcal

II. C-C bond energy : The heat of formation of ethane is −20.3 Kcal, *i.e.*,

$$\begin{array}{llll}
(i) & 2C\,(s) + 3H_2\,(g) = C_2H_6\,(g); & & \Delta H_f = -20.3 \\
(ii) & 2C\,(s) = 2C\,(g); & & \Delta H = 2 \times 170.9 \\
(iii) & 3H_2\,(g) = 6H\,(g); & & \Delta H = 6 \times 52.1
\end{array}$$

Rearranging (*i*), (*iv*) $C_2H_6\,(g) = 2C\,(s) + 3H_2\,(g)$; $\Delta H = 20.3$

Adding (*ii*), (*iii*) and (*iv*), $C_2H_6\,(g) = 2C\,(g) + 6H\,(g)$; $\Delta H = 6 \times 52.1 + 2 \times 170.9 + 20.3 = 674.7$ Kcal

That is, the energy for breaking one C-C bond and six C-H bonds = 674.7 Kcal

The bond-energy of 6 C-H bonds = $6 \times 99 = 594$ Kcal

$\therefore$ The C-C bond-energy = $674.7 - 594 \approx 81$ Kcal

III. C = C bond energy : This is also obtained in a similar fashion. The heat of formation of ethylene is + 12.5 Kcal. Therefore,

$$\begin{array}{llll}
(i) & 2C\,(s) + 2H_2\,(g) = C_2H_4\,(g); & & \Delta H_f = 12.5 \text{ Kcal} \\
(ii) & 2C\,(s) = 2C\,(g); & & \Delta H = 2 \times 170.9 \\
(iii) & 2H_2\,(g) = 4H\,(g); & & \Delta H = 4 \times 52.1
\end{array}$$

Rearranging (*i*), (*iv*) $C_2H_4\,(g) = 2C\,(s) + 2H_2\,(g)$; $\Delta H = -12.5$ Kcal

Adding (*ii*), (*iii*) and (*iv*) $C_2H_4\,(g) = 2C\,(g) + 4H\,(g)$;

$$\Delta H = 2 \times 170.9 + 4 \times 52.1 - 12.5 = 537.7 \text{ Kcal}$$

The energy of 4 C—H bonds = $4 \times 99 = 396$ Kcal

Hence, C = C bond energy = $537.7 - 396 = 141$ Kcal

The bond-energy (ϵ) of triple or double bonds is larger than that of the single bond. It has been estimated, the bond-energy ratio,

$$\epsilon_{c-c} : \epsilon_{c=c} : \epsilon_{c\equiv c} = 1 : 1.77 : 2.48$$

Similarly, for the C-O bonds,

$$\epsilon_{c-o} \text{ (alcohols)} : \epsilon_{c=o} \text{ (ketones)} = 1 : 2.12$$

In such calculations it is presumed that the C-H bond energy in methane, ethane, ethylene, etc. is the same. This is not strictly correct. The bond energy is subject to some variation due to environmental linkings. That is, the value of the bond energy depends upon the nature of the atoms linked with the neighbouring bonds and also to the stereochemistry of the molecule. The variation in the values is however often small.

A common illustration can be cited with pentanes. All the three isomeric pentanes have four C-C bonds and twelve C-H bonds and yet their energies differ :

		ΔH_0 (Kcal)
n-pentane,	$CH_3CH_2CH_2CH_2CH_3$	−30.15
Iso-pentane	$(CH_3)_2CH.CH_2CH_3$	−31.54
Neo pentane	$(CH_3)_4C$	−34.18

Determination of 'heat of reaction' and 'heat of formation' from bond-energy values : Using the bond energy-values, the heats of formation or heat of reaction can be computed. The results would be approximate as the bond-enthalpies are only average values.

Example (14) : Using bond-energy values from the table, calculate the heat of reaction for the following process :

$$CH_4(g) + Br_2(g) = CH_3Br(g) + HBr(g); \quad \Delta H = ?$$

The reaction involves the following processes :

(*i*) breaking 1 C − H bond, ΔH = 98.7 Kcal/mole

(*ii*) breaking 1 Br − Br bond, ΔH = 46.08 Kcal/mole

(*iii*) formation of 1 H − Br bond, ΔH = −87.4 Kcal mole

(*iv*) formation of 1 C − Br bond, ΔH = −74.0 Kcal/mole

$\Delta H_{\text{reaction}}$ = − 16.62. Kcal

Example (15) : Calculate the heat of formation of methyl alcohol from standard values of bond energies.

$$C(s) + 2H_2(g) + \tfrac{1}{2}O_2(g) = CH_3OH(l)$$

The energy changes are Kcal

(*i*) atomisation of carbon (1 mole) = 170.9

(*ii*) atomisation of 2 moles hydrogen = 4 × 52.1

(*iii*) atomisation of ½ mole oxygen = 59.6

(*iv*) formation of 3 C−H bonds = −3 × 99

(*v*) formation of 1 C−O bond = −84

(*vi*) formation of 1 O−H bond = −110.5

(*vii*) Liquefaction of 1 mole CH_3OH = −8.4

Adding ΔH = −61.0 Kcal

($\Delta H = \Sigma$ heats of atomisation − Σ Bond energies)

The heat of formation of the liquid alcohol is −61 Kcal/mole

If there exist one or more resonating structures in the substances considered, the resonance energy should also be taken into account.

Problems

1. Given

(*i*) $C_2H_4(g)+3O_2(g) = 2CO_2(g)+2H_2O(l)$; $\Delta H = -337$ Kcal

(*ii*) $H_2(g)+\frac{1}{2}O_2(g) = H_2O(l)$; $\Delta H = -68$ Kcal

(*iii*) $C_6H_6(g)+7/2.O_2(g) = 2CO_2(g)+3H_2O(l)$; $\Delta H = -373$ Kcal

Find out the heat of reaction of the process :

$C_2H_4(g)+H_2(g) = C_2H_6(g)$ **Ans.** -32 Kcal

2. 100 gm. of anhydrous $CuSO_4$ when dissolved in excess of water produced 10,000 calories of heat. The same amount of $CuSO_4, 5H_2O$ on dissolving in large excess of water absorbed 1,100 calories. What is the heat of hydration of $CuSO_4$? **Ans.** -18639 cal

3. Compute the heat of reaction for the following chemical change:

$$2CO\,(g) + 4H_2\,(g) = H_2O\,(l) + C_2H_5OH\,(l)$$

Given : Heats of combustion of H_2, CO, and C_2H_5OH as $-68.37, -67.64$ and -326.87 Kcal respectively. **Ans.** -81.9 Kcal

4. What amount of heat will be evolved if 1 m^3 of methane is completely burnt under normal conditions.

Given heats of formation of CH_4, CO_2 and H_2O (*g*) as ($\Delta H°_f$), -17.9, -94.05 and -57.79 Kcal respectively.

5. $\Delta H°_f(C_2H_5OH) = -66.3$ Kcal; $\Delta H°_f\,(H_2O)_l = -68.3$ Kcal and

$$\Delta H°_f\,(C_2H_4) = +12.5 \text{ Kcal}.$$

What is the standard heat of reaction for the process,

$C_2H_4\,(g) + H_2O\,(l) = C_2H_5OH\,(l)$? **Ans.** -10.5 Kcal

6. Given

$2C_6H_6\,(l) + 15O_2 = 12CO_2 + 6H_2O$, $\Delta H_{298} = -1598.7$ Kcal

$2C_2H_2\,(g) + 5O_2 = 4CO_2 + 2H_2O$, $\Delta H_{298} = -620.1$ Kcal

Evaluate the heat of formation of benzene from acetylene at 25°C.

Ans. -130.8 Kcal

7. The heat evolved in neutralisation of HCN solution with a strong alkali is 3.0 Kcal. Find out the heat of dissociation of HCN. **Ans.** 10.4 Kcal

8. The enthalpy of formation of ammonia (*g*) and hydrogen fluoride (*g*) are -46100 and -271100 joules. Show that in the reaction,

$$NH_3\,(g) + 3/2\,F_2\,(g) \rightarrow \tfrac{1}{2}N_2\,(g) + 3HF\,(g),$$

the heat of reaction is -767200 joules.

9. Calculate the theoretical temperature of the flame when acetylene would burn in the requisite amount of air.

Given : $C_P\,(N_2) = 6.45 + 1.4 \times 10^{-3}T$
$C_P\,(H_2O,g) = 7.22 + 2.4 \times 10^{-3}T$
$C_P\,(CO_2) = 6.4 + 10.1 \times 10^{-3}T$.

Ans. $T = 2450°K$.

Hints : The heat of combustion of acetylene is -310600 cal. That is,

$$C_2H_2 + \tfrac{5}{2}O_2 = 2CO_2 + H_2O; \qquad \Delta H = -310600 \text{ cal}$$

The gases present in the flame-zone after combustion are carbon dioxide, water vapour and the unreacted nitrogen of the air. Since 5/2 moles of oxygen were required for combustion, nitrogen present would be approximately 10 moles. Hence the composition of the resultant gases would be 2 moles CO_2, 1 mole H_2O vapour and 10 moles nitrogen. The heat-capacities of these gases *approximately* are :

$$2 \times C_{P_{CO_2}} = 2(6.4 + 10.1 \times 10^{-3}T) = 12.8 + 20.2 \times 10^{-3}T$$

$$C_{P_{H_2O}} = 7.22 + 2.4 \times 10^{-3}T$$

$$10 \times C_{P_{N_2}} = 10(6.45 + 1.4 \times 10^{-3}T) = 64.5 + 14 \times 10^{-3}T$$

$$\therefore \ \Sigma \nu C_P = 84.52 + 36.6 \times 10^{-3}T$$

Hence,

$$\Delta H = \int_{298}^{T} \Sigma \nu C_P \, dT$$

10. With the aid of bond energies from the table, estimate the heat of reaction of the following change :

$$CH_3COCH_3 + 2O_2 = CH_3COOH + H_2O + CO_2$$

11. The heats of atomisation of nitrogen and hydrogen are 113 and 52.1 Kcal. The bond-energy (N$-$H) = 93.3 Kcal. Calculate the heat of formation of ammonia.

12. Estimate the heats of the following gaseous reactions, using standard bond-energy values, ignoring resonance if any.

(*i*) $CH_4 + Cl_2 = CH_3Cl + HCl$; (*ii*) $2C_8H_{18} + 25O_2 = 16CO_2 + 18H_2O$

13. At 17°C, at constant pressure, the heat of combustion of amorphous carbon is -96960 cal and that of CO to CO_2 is -67960 cal. Determine the heat of formation of CO at constant volume **Ans.** -29290 cal

14. Acetylene burns with a brilliant flame in N_2O gas producing a high temperature. The reaction is

$$C_2H_2 + 3N_2O = 2CO + H_2O + 3N_2$$

Calculate the maximum flame temperature.

Given enthalpies of formation :

$$\Delta H_{f(CO)} = -110.5, \ \Delta H_{f(H_2O)} = -241.8, \ \Delta H_{f(C_2H_2)} = +226.7 \text{ kj}$$

$$\Delta H_{f(N_2O)} = +82.05 \text{ kj}$$

For heat-capacity values, standard tables may be consulted.

Ans. $T = 4300$°K approx.

15. Calculate the energy of C$-$S bond in CS_2. Given, molar heats of combustion of CS_2 (*l*), C(*s*) and S(*s*) are -265 Kcal, -94 Kcal and -71 Kcal respectively. The molar heats of atomisation for C(*s*) and S(*s*) are 170 Kcal and 67 Kcal respectively. The latent heat of vaporisation of CS_2 is 6.4 Kcal.

Ans. 134.1 Kcal

CHAPTER 4

THE SECOND LAW

4-1. The need for the second law

The first law summarizes our experience regarding the transformation of energy. We have learnt that (*i*) the different forms of energy are interconvertible and (*ii*) when one form of energy disappears an equivalent amount of another kind must appear. But there is an elememt of incompleteness in the First Law. The First Law does not indicate whether the change would at all occur and, if it occurs, to what extent. Moreover, it also does not indicate the direction in which the change would take place.

To illustrate : (*a*) Suppose two bodies A and B are brought in contact. Then from the first law, we only know if q calories of heat are lost by A, exactly q calories of heat would be gained by B, or *vice versa*. But the law does not state if A or B would lose the heat energy. To know the direction of flow of heat we need another information, namely, the temperatures of A and B.

(*b*) Again, consider the chemical change, $PCl_5 = PCl_3 + Cl_2$: the first law tells us only that if z calories of heat be evolved during the dissociation of pentachloride, then in the opposite reaction of combination of trichloride and chlorine exactly z calories of heat would be absorbed. But if we have an arbitrary mixture of PCl_5, PCl_3 and Cl_2, we cannot ascertain from the first law alone if there would be dissociation of pentachloride or not. To determine the direction in which the chemical change would occur, we require the knowledge of the equilibrium constant of the reaction.

(*c*) A copper and a zinc rod partially immersed in dilute sulphuric acid and externally connected will transform chemical energy to electrical energy. But whether the current will flow from copper to zinc or *vice versa* cannot be determined unless we are aware of the electrode potentials of the two metals.

These amply illustrate the insufficiency of the first law. To ascertain the direction of a chemical or a physical process we need some more information or the knowledge of some other criteria beyond the first law. The principle which would determine the direction as also the extent of a change is provided by the Second Law. Like the first law, the Second Law is also truly a law of experience gathered from observations of nature. Any such experience which would determine the criteria for the direction for the occurrence of a change will be the basis of the Second Law. These experiences have been expressed in different ways by different workers. That is why we often find a large number of statements for the Second Law, though all of them lead to the same goal, namely to indicate the direction of a process.

4.2. Spontaneous processes

Changes taking place in a system without the aid of any external agency are termed *spontaneous processes*. We shall make an attempt here to collect experiences with some very simple spontaneous processes.

(*i*) Suppose a vessel containing a gas at higher pressure P_1 be connected by a tube to another vessel where the pressure is less, say P_2; $(P_1 > P_2)$. It is our experience that the gas would spontaneously move from the higher to the lower pressure. This process would continue until the two pressures are equalised and a *mechanical equilibrium* is established. Further we find that the change is unidirectional *i.e.*, irreversible. When equilibrium is attained, the gas, by itself, will not rush back to the first vessel to increase the pressure to its original higher value.

(*ii*) If solutions of two different concentrations be brought in contact, the solute begins to diffuse from the higher to the lower concentration till the concentration throughout becomes the same. This spontaneous action is also unidirectional and would continue till the *equilibrium* is reached. Further, by itself the solute would not migrate back to make one portion more concentrated than the rest.

(*iii*) If a hotter body *A* at temperature T_1 comes in contact with a colder body *B* at temperature T_2, $(T_1 > T_2)$, we always find heat flowing from *A* to *B* until the temperatures of both *A* and *B* become equal, *i.e.*, a *thermal equilibrium* is attained. Here also, heat does not flow from *B* to *A*, *i.e.*, the transfer is unidirectional and irreversible. After attaining equilibrium, *B* would not spontaneously become cooler making *A* warmer until their original temperatures are restored, though such a step would not violate the first law.

(*iv*) It is a common experience that a liquid will always flow freely from a higher to a lower level until the levels are equalised, *i.e.*, *mechanical equilibrium* is reached. This is also an irreversible process.

(*v*) Metallic copper is deposited with evolution of heat when copper sulphate solution is brought in contact with zinc, and the reaction continues until the *chemical equilibrium* is attained. The broad fact is that a chemical reaction would always proceed in a direction to reach the equilibrium.

Many other examples may be given. But all these spontaneous processes take place in one direction and are irreversible. Every system naturally moves towards the equilibrium state. The Second Law which is formulated to record our experience about the direction of changes, may therefore be stated as,

"*All spontaneous processes are irreversible.*"

and we may further add,

"*All spontaneous processes tend to equilibrium.*"

If we confine our attention to a specific case, namely the flow of heat as in our illustration (*iii*), we can express our experience by the statement given by Clausius,

"*Heat, of itself, will not pass from lower to a higher temperature.*"

Or, more elegantly stated;

"*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from a body at a low to one at a high temperature.*"

Another aspect of the spontaneous processes must also be considered. In all these spontaneous changes, outside effort would be required to effect the reverse change. To take the water to a higher level, to separate the solute from the solution, to produce back the zinc from the solution of zinc sulphate and copper etc., work must be done on the system.

On the other hand, during the spontaneous occurrence of natural processes, seldom any energy is obtained in useful form or work. But nevertheless, by the introduction of suitable mechanisms, it is possible to obtain useful work when spontaneous processes move towards equilibrium. The mechanism employed to obtain the work may differ from process to process. Thus, the flow of water downwards would yield work if a turbine is installed; the flow of heat from higher to lower temperature produces work if a heat engine be employed ; the reaction between copper sulphate and zinc would give useful work through a galvanic cell ; the movement of gas from a higher to a lower pressure can be made to do work through a wind-mill etc.

4.3. The second law of thermodynamics

We have indicated in the previous section the basis of the second law for the guidance of a process in a definite direction. It is also a human experience that when every form of energy, including mechanical work, has a natural tendency to be transformed into thermal energy, the latter shows no natural inclination to be transformed into any other form. Only through the introduction of some mechanism, or machine, can we convert heat into other forms. Even then this conversion occurs to a limited extent and not completely. Since heat is readily available, a good deal of human ingenuity is employed to find out the conditions and circumstances under which it would be possible to change heat into work. The guidance as to the conditions under which heat changes into the direction of work would obviously come under the Second Law. For this reason, in enunciating the Second Law we often find the statements refer to the conversion of heat into work. It is now known that two conditions must be fulfilled to utilise heat for useful work.

1. A contrivance or mechanism, commonly called the "thermodynamic engine", is essential. Without the aid of an engine the conversion of heat into work is impossible. Further, the engine must work in a reversible cyclic process.

2. The engine must operate between two temperatures. It will take up heat at a higher temperature, convert a portion of it into work and give up the rest of the heat to a body at a lower temperature.

Now suppose we have, for an engine, a cylinder with a piston containing x gm-moles of an ideal gas, at temeperature T same as that of the surroundings. Let the gas expand isothermally from a volume V_1 to a volume V_2. There would be no change in internal energy, for the gas is ideal. The heat absorbed from the surroundings will be completely converted into work dW, $\left(= xRT \ln \frac{V_2}{V_1}\right)$, in accordance with the first law. Here is then a case where Q quantity of heat from the surroundings is completely converted into work, W. But when this has been achieved, the external agency, (the engine), has suffered a change in volume from V_1 to V_2. It is thus an experience that *complete conversion of heat into work is impossible without leaving a permanent change elsewhere.*

If we want to repeat the performance, the gas must be made to come back to its original volume and pick up heat again from the surroundings during expansion. To bring the gas to its original volume V_1 from V_2, we must perform isothermal work of compression equal to $- xRT \ln \frac{V_2}{V_1}$, the same that we obtained before. The net result is that the engine, working in a cycle at a temperature same as that of the source of supplier of heat (in this case of the surroundings), would produce no work. It is now a fundamental fact of experience that *under isothermal conditions no engine can convert heat into work.* That is why we cannot run our tram cars or motor cars with the heat of the surrounding air, or we cannot utilise vast amounts of ocean-heat to move our ships.

This was stated by Clausius as : "*It is impossible to construct a device operating in a cycle which will produce no effect other than the transfer of heat from a body to another at a higher temperature.*

The same was stated by Planck and he defined the second law as,

"*It is impossible to construct an engine, working in a cycle, which would produce no effect except the raising of a weight and the cooling of a heat reservoir.*"

In other words, no process can be realised in which the *sole result* would be the absorption of heat from a reservoir and the complete conversion of the same into work. No engine can produce work from a single source of heat.

If a machine could be produced which would continuously take up heat from a single reservoir (thereby gradually cooling the reservoir) and convert it into work, we would achieve what is called the 'perpetual motion of the second kind'.

Such a machine installed in our drawing room would take up heat from the air of the room and perform the mechanical work of running the fan. The air of course, will automatically cool due to loss of heat. Hence no supply of electric energy from the electric supply company would be needed. The operation of a machine which utilises the heat energy of a single heat reservoir to produce work can never be realised. All attempts to produce such a perpetual motion machine of the second kind have failed and is contrary to experience. Therefore Ostwald said : "*It is impossible to construct a perpetual motion machine of the second kind.*"

Kelvin stated the Second law in the form :

"*It is impossible by an inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surroundings.*"

If such a machine could be evolved then perpetual motion of the second kind could be realised, but that is not possible.

All these statements make a specific reference of a machine or an engine, without which the transformation of heat into work is not possible. Further, we have seen that the heat obtained from a supplier at the same or lower temperature than that of the engine cannot be transformed into work in a cyclic process. But when heat flows from a reservoir at a higher temperature (called the *source*) to a reservoir at a lower temperature (called the *sink*), it can be transformed into work with the intervention of an engine. The engine would pick up Q calories of heat from the source, transform only a portion of it into work W and return the rest of the heat Q' to the sink. According to the first law then

$$W = Q - Q'$$

The amount of work obtained from a given amount of heat (Q) depends on the temperatures of the source and the sink and on the nature of the engine. It should be realised that though the conversion of heat into work is partial, it does not violate the principle of the First Law.

The efficiency (η) of the engine is defined in the usual way ;

$$\eta = \frac{\text{work produced}}{\text{energy supplied}} = \frac{W}{Q} = \frac{Q-Q'}{Q} \qquad \ldots (4.1)$$

or $$\eta = 1 - \frac{Q'}{Q} \qquad \ldots (4.2)$$

Its utility, in practice, can be realised by considering a cyclic process with a machine working between two temperatures. The most ideal of such cyclic processes would be the *Carnot Cycle*.

4.4. Carnot Cycle

In the beginning of the nineteenth century, quite a number of heat-engines were in use but the priniciple which governed the conversion of heat into work in those engines was not clearly understood. It was the brilliant young French engineer Sadi Carnot (1824) who explained clearly how and to what extent work is obtainable from heat. Carnot started with two essential prerequisites. Firstly, to estimate the work obtained from heat during its passage from higher to lower temperature, the external agency (the engine) must come back to its original state so as to exclude any work involved in its own change. That is, the engine must perform in complete cycles. Secondly, to obtain maximum work in a cycle of operations, every step should be carried out in a reversible fashion.

The typical Carnot cycle consists of four successive operations using one mole of an ideal gas as the working substance. The gas is enclosed in a cylinder fitted with a frictionless piston. [The cylinder with the enclosed gas serves as the thermodynamic engine].

There are two thermostats or heat reservoirs—one at a higher temperature T (source) and the other at a lower temperature T' (sink). To start with, the cylinder containing the gas under pressure P_o and of volume V_o, is kept in the lower temperature bath (T'). The gas is then subjected to two alternate adiabatic and two isothermal expansion (or contraction) as follows. At the end of the four such processes, the engine returns to its initial state.

Operation 1. The gas at T' is adiabatically and reversibly compressed until its temperature rises to T (the temperature of the source) and the volume changes from V_0 to V_1.

The heat absorbed by the gas = nil

or the work done by the gas $= -C_V(T-T')$

(C_V is the heat-capacity of the gas)

Operation 2. The cylinder, containing the gas having volume V_1 and temperature T, is now placed in a large thermostat (source) of temperature T. The gas is allowed to expand reversibly and isothermally from volume V_1 to V_2.

The heat absorbed during the expansion = Q (say)

The work done by the gas $= RT \ln \frac{V_2}{V_1}$

Since the gas is an ideal one, we have from the First Law,

$$Q = RT \ln \frac{V_2}{V_1} \quad \ldots (4.3)$$

Operation 3. The cylinder is next taken out of the thermostat and kept in a thermally insulated enclosure. The gas is then allowed to expand further adiabatically and reversibly until the temperature falls down to orignial initial temperature T'. The volume of the gas would change from V_2 to V_3 (say).

The heat absorbed by the gas = nil

The work done by the gas $= C_V(T-T')$

Operation 4. The cylinder is now placed in a large thermostat (sink) of temperature T'. The gas is then subjected to an isothermal reversible compression until the volume reduces from V_3 to V_0 (the initial volume and temperature).

The heat given out by the gas $= Q'$ (say)

The work done by the gas $= RT' \, ln \, \frac{V_0}{V_3}$

[Since V_0 is less than V_3, the work is negative *i.e.* it is done on the gas.]

The engine has returned to its initial state and the cycle is completed.* Some changes have taken place in the surroundings. The operations may be represented conveniently in a P-V diagram as in Fig. 4*a*. In this diagram D is the initial starting point with volume V_o and pressure P_o at temperature T'. DA and BC donote the adiabatic compression and expansion respectively, whereas AB and CD are the isothermal expansion and compression respectively. The enclosed area ABCD represent the work obtained in the complete cyclic process.

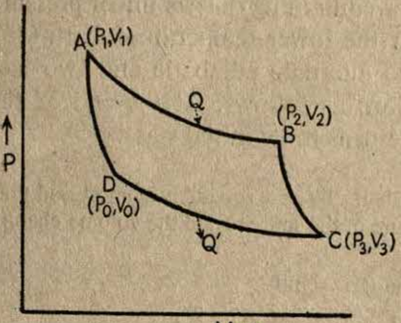


Fig 4*a*. The Carnot Cycle

The net work done by the gas in the complete cycle,

$$W = -C_V(T-T') + RT \ln \frac{V_2}{V_1} + C_V(T-T') + RT' \ln \frac{V_o}{V_3}$$

$$= RT \, ln \frac{V_2}{V_1} - RT' \, ln \frac{V_3}{V_o}$$

But in the adiabatic operations, since $TV^{\gamma-1} =$ constant, we have

(*i*) $TV_2^{\gamma-1} = T'V_3^{\gamma-1}$

and (*ii*) $TV_1^{\gamma-1} = T'V_o^{\gamma-1}$

Dividing, $\frac{V_2}{V_1} = \frac{V_3}{V_o}$

Hence the net work, $W = RT \, ln \frac{V_2}{V_1} - RT' \, ln \frac{V_2}{V_1}$

$$= R(T-T') \, ln \frac{V_2}{V_1} \qquad \ldots (4.4)$$

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* M. N. Das, Indian J. chem. Edn, 1978, 5, 16.

The efficiency, $$\eta = \frac{W}{Q} = \frac{R(T-T')\ ln\frac{V_2}{V_1}}{RT\ ln\frac{V_2}{V_1}}, \text{ (from eqn. 4.3)}$$

$$= \frac{T-T'}{T} = \frac{\triangle T}{T} \qquad \ldots (4.5)$$

Hence, $$W = Q\frac{\triangle T}{T} \qquad \ldots (4.6)$$

This relation expresses the maximum amount of work obtainable from the heat flowing from T to T'. The work obtainable depends on the temperatures of the source and the sink. This is the mathematical form of the Second Law. (The same result would be obtained even if the cycle started from some other point.)

The efficiency, $$\eta = \frac{T-T'}{T}$$

or $$\frac{W}{Q} = \frac{T-T'}{T}$$

i.e., $$\frac{Q-Q'}{Q} = \frac{T-T'}{T}$$

hence $$\frac{Q}{Q'} = \frac{T}{T'} \text{ or } \frac{Q}{T} = \frac{Q'}{T'} \qquad \ldots (4.7)$$

Notes : (*i*) Between two given temperatures, only $\triangle T/T$ fraction of the total heat supplied at T is transformed into work. The rest of the heat is released to the sink and cannot be rendered into work. Though heat is present, it is not available as work. This unavailability is hence regarded as *degradation of energy* as heat passes from a higher to a lower temperature.

(*ii*) $W = Q$, only when $T' = 0$. That is, if the engine works between absolute zero and a higher temperature, complete conversion of heat into work would be possible. Since working an engine at 0°K cannot be realised in practice, the complete transformation of heat into work is impracticable ; the efficiency is thus always less than unity.

(*iii*) The efficiency of the engine depends only on the temperatures of the source and the sink (eq. 4.5). For a given source, the lower the temperature of the sink the greater will be the yield of work. Very often the sink is at the room temperature. In such a case, for greater output of work, the temperature of the source should be high. This is the reason for using high pressure steam in boilers for production of power.

(*iv*) When $T = T'$, work W becomes zero. No work is available by operating an engine under isothermal conditions.

(*v*) The ratio of the volumes after adiabatic expansion and before *i.e.*, $\frac{V_3}{V_2}$ is called the adiabatic *expansion ratio*, denoted by ρ.

We have seen in the Carnot cycle that

$$T'V_3^{\gamma-1} = TV_2^{\gamma-1}$$

or
$$\frac{T'}{T} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{1}{\rho}\right)^{\gamma-1}$$

Hence the efficiency, $$\eta = 1 - \frac{T'}{T} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad \ldots (4.8)$$

Example (1) : A Carnot engine working between 0°C and 100°C takes up 840 joules from the high temperature reservoir. Calculate the work done, the heat rejected and the efficiency.

(*a*) Work done $W = Q_1 \times \frac{\Delta T}{T} = 840 \times 10^7 \times \frac{100}{373} = 2.25 \times 10^9$ ergs $= 0.225$ kj

(*b*) Heat rejected $Q_2 = Q_1 \cdot \frac{T_2}{T_1} = \frac{840}{4.2} \cdot \frac{273}{373} = 146$ calories

(*c*) Efficiency, $\eta = \frac{T_1 - T_2}{T_1} = \frac{100}{373} = 0.268$

Example (2) : An engine works in a Carnot's cycle between 27°C and 127°C and the work output per cycle is 300 Kgm-metres. Calculate the heat supplied to the engine from the source.

Let heat supplied $= Q$ calories.

Since $$W = Q\,\frac{\Delta T}{T},$$

Expressed in ergs, $300 \times 1000 \times 100 \times 981 = Q \times 4.2 \times 10^7 \times \frac{100}{400}$

or $$Q = 2803 \text{ calories.}$$

4.5. The Carnot Theorem

This theorem embodies two important deductions derived from the Second Law. These are,

(*i*) *a reversible engine is more efficient than an irreversible one* and

(*ii*) *all reversible engines are equally efficient working between the same temperature limits.*

We can proceed to establish them in the following way. (*i*) Suppose we have an irreversible engine *I* and a reversible engine *R*. Let us assume the efficiency of *I* greater than that of *R*, *i.e.*, $\eta_I > \eta_R$. This means that if a source supplies same quantity of heat to both the engines, greater amount of work will be obtained from *I* than from *R*. Suppose the engines operate between the source at temperature *T* and the sink at temperature *T′*. Now the energy changes with the two engines would be as follows :

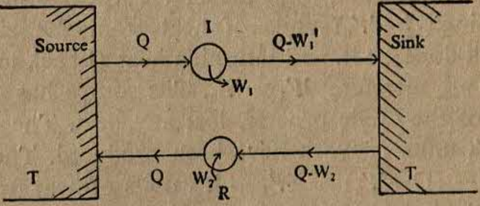


Fig. 4*b*

Engine *I*

Heat supplied by source $= Q$
Work performed $= W_1$
Heat rejected to sink $= q_1$, $(q_1 = Q - W_1)$

Engine *R*

Heat supplied by source $= Q$
Work performed $= W_2$
Heat rejected to sink $= q_2$, $(q_2 = Q - W_2)$

We know, $W_1 > W_2$ and hence, $Q - W_1 < Q - W_2$, or $q_2 > q_1$

Let us now carry out a cyclic process in which the irreversible engine *I* would perform the forward process. It is supplied with heat *Q* from the source and it yields W_1 work and reject the rest of the heat q_1 $(= Q - W_1)$ to the sink (Fig. 4*b*).

The reverse process is carried out by the reversible engine *R*. Since it is reversible, it will take up heat q_2 $(= Q - W_2)$ from the sink and having W_2 units of work done on it return heat *Q* to the source. In this complete cyclic process, the source has not lost any heat. But the coupled engines have yielded

$$\text{net work} = W_1 - W_2.$$

The sink has received q_1 heat and lost q_2 heat and since $q_2 > q_1$. The sink has a net loss of heat $= q_2 - q_1 = (Q - W_2) - (Q - W_1)$

$$= W_1 - W_2$$

That means we have been able to convert completely the heat taken from the single reservoir sink at the lower temperature. This is impossible. Hence an irreversible engine cannot be more efficient than a reversible engine.

(*ii*) The second part of the theorem can also be proved in a similar way. Suppose two reversible engines R_1 and R_2 work between the source (T) and the sink (T'). If possible, let us assume, one of the engines, say R_1, is more efficient than R_2. As before, let us couple the two engines to carry out a cyclic process. The engine R_1 takes up heat Q from the source, yields work W_1 and rejects $(Q-W_1)$ heat to the sink, while the engine R_2 perform the opposite process, taking $(Q-W_2)$ units of heat from the sink with W_2 units of work done on it, and returning heat Q back to the source. Since $\eta_{R_1} > \eta_{R_2}$ therefore $W_1 > W_2$. The source has not, at the completion of the cyclic process, lost any heat. The net result is that $W_1 - W_2$ units of work have been produced. There is a loss of $(Q-W_2) - (Q-W_1) = W_1 - W_2$ units of heat from the sink. The heat of the lower temperature sink is thus completely converted into work, which is against the Second Law. Thus, engine R_1 cannot be more efficient than R_2. Similarly, R_2 also cannot have greater efficiency than R_1. That is, both the engines are equally efficient. Hence all reversible engines working between the same temperatures must be equally efficient. Since we have not taken into consideration the nature of the working substance of the engine, we may also say that the efficiency of the Carnot engine is *independent of the nature of the working substance.*

4-6. Kelvin Scale of Temperature

The mesurement of tempertature is based on some property of the thermometric substance, such as linear or volumetric expansion, electrical resistance, etc. But the variation in the property studied is not exactly the same for different substances, nor is it regular in different ranges of temperature. In measuring T_1/T_2, the ratio of temperatures of two given reservoirs, with a constant-volume nitrogen thermometer and a constant-volume helium thermometer, the readings would be slightly different.

We have seen that the efficiency of the reversible engine is dependent only on the temperature of the source and the sink and is independent of the materials used. In a Carnot cycle,

$$\eta = \frac{Q-Q'}{Q} = \frac{T-T'}{T}; \qquad \text{hence, } \frac{Q}{Q'} = \frac{T}{T'}$$

where Q and Q' are heat received from the source at T and heat given up to the sink at T respectively. T and T' are expressed in ideal gas scale.

Kelvin proposed that a knowledge of the quantities of heat Q and Q' would be possible to define a scale of temperature independent of any property of the substance. It would then be a *thermodynamic scale* of measurement in which thermometry would be replaced by calorimetry.

Let us take three reservoirs (A, B and C) in decreasing order of temperatures. Let us also denote by the symbol, τ, a quantity which is a measure of the temperatures or levels of hotness of the reservoirs (Fig. 4*c*).

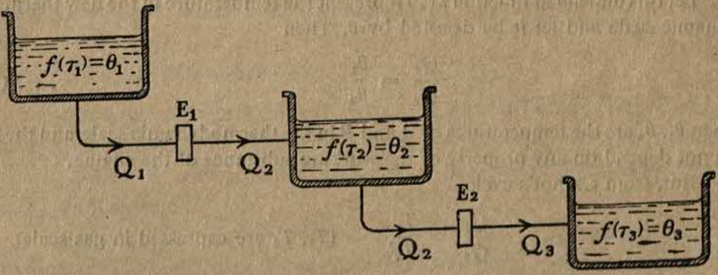


Fig. 4*c*

Suppose a Carnot engine (E_1) works between the reservoirs A and B receiving Q_1 heat from A and rejecting Q_2 heat to B. Then, the ratio Q_1/Q_2 will be a function of temperatures of A and B, *i.e.*, a function of τ_1 and τ_2.

So, $$\frac{Q_1}{Q_2} = F(\tau_1, \tau_2) \qquad \ldots (i)$$

the nature of the function need not be prescribed now.

If now, a second Carnot engine (E_2) works between B and C, taking Q_2 heat from B and rejecting Q_3 heat to C,

then, $$\frac{Q_2}{Q_3} = F(\tau_2, \tau_3) \qquad \ldots (ii)$$

Now let the two engines be put in series to work between the baths A and C. Then we would have,

$$\frac{Q_1}{Q_3} = F(\tau_3, \tau_2) \qquad \ldots (iii)$$

Dividing (*iii*) by (*ii*), $$\frac{Q_1}{Q_2} = \frac{F(\tau_1, \tau_3)}{F(\tau_2, \tau_3)} \qquad \ldots (iv)$$

Comparing (*i*) and (*iv*), $$F(\tau_1, \tau_2) = \frac{F(\tau_1, \tau_3)}{F(\tau_2, \tau_3)}$$

The left-hand side of this equation does not contain τ_3, which occurs only on the right-hand side. This is possible only if the form of the function F is a ratio function and of identical nature in both the numerator and the denominator *i.e.*,

$$F(\tau_1, \tau_2) = \frac{f(\tau_1)}{f(\tau_2)} \quad \text{and} \quad F(\tau_2, \tau_3) = \frac{f(\tau_2)}{f(\tau_3)}$$

Then, $$F(\tau_1, \tau_2) = \frac{F(\tau_1, \tau_3)}{F(\tau_2, \tau_3)} = \frac{f(\tau_1)}{f(\tau_3)} \times \frac{f(\tau_3)}{f(\tau_2)} = \frac{f(\tau_1)}{f(\tau_2)}$$

Hence, from (*i*) $$\frac{Q_1}{Q_2} = \frac{f(\tau_1)}{f(\tau_2)}$$

Let this undefined function $f(\tau)$ represent the temperature in the new thermodynamic scale and let it be denoted by θ. Then

$$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2} \qquad \ldots (v)$$

when θ_1, θ_2 are the temperatures of A and B in the thermodynamic scale and these do not depend on any property of the working substance of the engine.

But, from Carnot's cycle,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}, \qquad (T_1, T_2 \text{ are expressed in gas scale}).$$

$$\therefore \quad \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2}, \text{ or } \theta = kT, \text{ (where } k \text{ is a constant)} \ldots (vi)$$

The freezing pt. and boiling pt. of water in the two scales are θ_f, θ_b and T_f, T_b

$$\therefore \quad \frac{\theta_b}{\theta_f} = \frac{T_b}{T_f} \qquad \ldots (vii)$$

For the magnitude of the unit degree in the themodynamic scale, Kelvin proposed the range between freezing and boiling points of water to be divided in 100 degrees, to make each degree equal to a centigrade degree. Then,

$$\theta_b - \theta_f = T_b - T_f = 100$$

Applying (*vii*), $$\frac{T_b}{T_f}.\theta_f - \theta_f = T_b - T_f$$

or $$\theta_f \frac{(T_b - T_f)}{T_f} = T_b - T_f$$

or $$\theta_f = T_f, \text{ and so, } \theta_b = T_b$$

That is, the constant in (*vi*) is unity, or, $\theta = T$.

The temperature in the gas scale and in the thermodynamic scale would be the same.

Further, since $$\frac{Q_1}{Q_2} = \frac{\theta_1}{\theta_2}$$

the efficiency, $$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\theta_1 - \theta_2}{\theta_1}$$

Hence if $\theta_2 = 0$, $\eta = 1$

The zero of thermodynamic scale has been defined to be the temperature of the sink working down to which the engine would completely convert heat into work. We have seen previously the same criterion for the absolute zero of temperature in the gas scale. Hence the zero of the two scales are identical.

To honour this fundamental contribution of Lord Kelvin the thermodynamic scale is called the *Kelvin Scale* with symbol °K.

4.6*a*. Clausius Inequality

This concept stems directly from the Second Law. The Clausius inequality states : "*The cyclic integral of the quantity $\delta q/T$ for a closed system is always equal to or less than zero.*" It may be established as follows:

Consider a system B (Fig $4c_1$) at temp. T operate in cycles. In its cyclic operations, it receives heat δQ from a high-temperature reservoir C maintained at constant temperature T_o. Suppose the system B produces work δW per cycle. Then from the First Law

$$\oint dQ = \oint dW \qquad \ldots (i)$$

To provide reversible supply of heat from C, insert a reversible engine R in between the system B and reservoir C. Let the engine make an integral number of cycles to one of B.

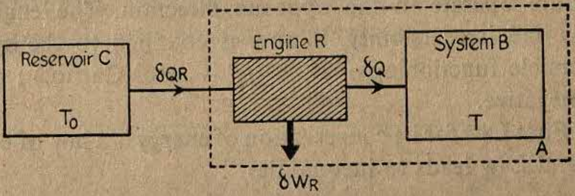


Fig. $4c_1$

The engine receives heat δQ_R from the source, performs δW_R work and delivers δQ heat to the system B. Then, for the reversible engine,

$$\frac{\delta Q_R}{T_o} = \frac{\delta Q}{T}; \text{ or } \delta Q_R = T_o \frac{\delta Q}{T} \qquad \ldots (ii)$$

Again, we have,

$$\delta Q_R = \delta Q + \delta W_R \text{ ; or } \delta W_R = \delta Q_R - \delta Q$$

$$\text{or } \delta W_R = T_o \frac{\delta Q}{T} - \delta Q \qquad \ldots (iii)$$

Now suppose the engine and the system B together form a composite system A. Then, the total work from this system A for each cycle of B, will be given by,

$$\oint dW_A = \oint(\delta W_R + \delta W)$$

$$= \oint\left(T_o\frac{\delta Q}{T} - \delta Q + \delta Q\right)$$

$$= \oint T_o\frac{\delta Q}{T} \qquad [\text{from } (iii)\ \&\ (i)]$$

But this composite system A operates in a cycle which exchanges heat with a single reservoir. Such a device, according to the Second Law, cannot produce work. However, there is no restriction where the work is equal to or less than zero. That is, the second Law requirement on cyclic heat-engines is governed by the fact that

$$\oint\delta W_A \leqslant 0$$

Hence, $\oint T_o\frac{\delta Q}{T} \leqslant 0$

Since T_o is constant and positive, $\oint\frac{\delta Q}{T} \leqslant 0$

This is known as *Clausius Inequality*. It is immaterial if the cycle would operate in the opposite direction. The engine R is reversible and irreversibility, if any, is confined to the system B. For reversible functioning of B, $\delta Q/T$ is zero (Carnot) ; otherwise $\delta Q/T$ is negative.

The First Law for its conservation of energy is a law of equalities. The Second Law leads to inequalities.

Common Heat Engines. The engines most commonly used for the generation of power are of two types ; (*i*) *steam engines and* (*ii*) *internal combustion engines.* We shall present here only a simplified outline of the principles on which these engines operate without entering into engineering details. We shall also ignore the complications that arise during the operation due to heat-transfers by friction, conduction, turbulence etc.

4.7. Steam Engines

Steam Engines. Water and its vapour are the working substance in these engines. The principle is to allow water to vaporise in a boiler taking up heat from a high temperature source (say, a furnace). The vapour is then allowed to expand adiabatically pushing out a piston or moving a turbine (thus, doing work) and simultaneously it is cooled to the temperature of the sink. The vapour is then condensed isothermally and finally the water is returned back to the boiler by adiabatic compression. The cycle is thus completed. The choice of water as the working substance is primarily due to its high latent heat of vaporisation, which enables it to take up larger quantities of heat from the source and its non-corrossive nature. Working between the same temperature-ranges Carnot's cycle would be the most efficient. Carnot's cycle however demands that every step should be perfectly reversible and that heat-exchanges in the source and in the sink must take place at constant temperatures. The realisation of these conditions in practice is of course almost impossible. The Carnot's cycles are therefore only ideal ones. The cyclic operations carried out in real heat-engines are an effort to reach this ideality. The efficiency of the Carnot's steam-engine working between the room temperature (say 27°C) and the boiling temperature (100°C) would be

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{373 - 300}{373} = 0.196$$

i.e., only 19.6% of the heat would be available as work. Increase of boiler pressure will raise its temperature yielding superheated

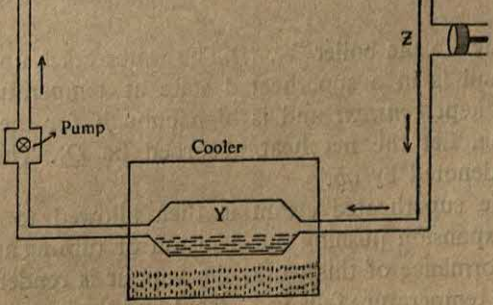
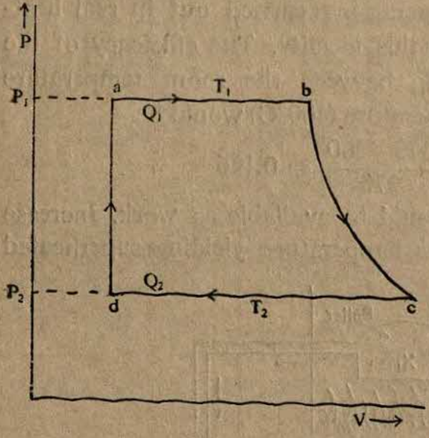


Fig. 4*d*. Operation of Steam power cycle

steam. Such rise of temperature will increase the work output. This advantage is taken of in the *Rankine cycles*, on the basis of which the steam plants are operated.

4.8. Rankine Cycle

The Rankine cycle is a model one for a steam power plant. The working substance (water) appears both in liquid and vapour phases during the cyclic process. The Rankine cycle follows the Carnot cycle and for simplicity, it is treated here as an idealised system. The schematic representation of the process is given in Fig 4*d* and the changes are graphically presented with *P-V* diagrams in Fig 4*e*. [A *T-S* representation is salso presented in Fig 4*f*]. We start from the point '*a*' (in Fig 4*e*) which corresponds to a given mass of water in the boiler X_1. (*i*) The water takes up latent heat, vaporises and is in a superheated state at temperature T_1. The pressure is kept *constant* and is high enough for the purpose of superheating. Let the net heat absorbed be Q_1. The change in volume is denoted by *ab*.



Fig, 4*e*. Rankine cycle (idealised)

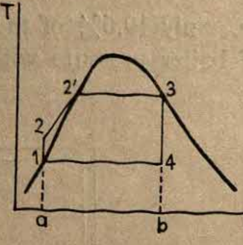


Fig. 4*f*. Rankine Cycle

(*ii*) The superheated steam is then allowed to undergo an adiabatic expansion pushing out a piston or turning a turbine (*Z*). In the performance of this work, the vapour is rendered into wet steam. The temperature falls to T_2 (say) and the pressure to P_2.

(*iii*) Under isobaric and isothermal condition the steam is condensed to saturated water at T_2. The change in volume is given by *cd*. The heat Q_2 is rejected to the cooler.

(*iv*) Finally, the water is adiabatically compressed from pressure (P_2) to the pressure (P_1) of the boiler and transferred there along *da*. The change in volume is negligible.

The cycle is completed and the net-work available is represented by the area *abcd*.

The efficiency of the cycle may be calculated approximately. Let H terms denote the enthalpies of the water or its vapour at different stages. Then the flow of heat into the engine at T_1, and the rejection of heat at T_2 are,

$$Q_1 = H_b - H_a \quad \text{and} \quad Q_2 = H_c - H_d$$

In passing along *da*, work is performed on the system in compressing the mass of water from P_2 to P_1 adiabatically. If V be the volume of the mass of water (practically constant), then

$$H_a - H_d = \int_b^a VdP = V[P_1 - P_2]$$

$$\text{The efficiency, } \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{H_b - H_a - H_c + H_d}{H_b - H_a}$$

$$= \frac{H_b - H_c - (H_a - H_d)}{H_b - H_d - (H_a - H_d)} = \frac{H_b - H_c - V(P_1 - P_2)}{H_b - H_d - V(P_1 - P_2)} \quad \ldots (4.9)$$

The heat-content values are available from steam-tables.

Example : In a Rankine cycle, steam saturated at 130 psia is expanded to a pressure of 15 psia. Determine the net-work of the cycle and its efficiency.

[From the steam tables, the following data are available per lb of water or steam. Under isoentropic condition,

(*i*) at 130 psia, enthalpy of sat. steam, H_b = 1191.7 Btu/1b.
(*ii*) at 15 psia, enthalpy of sat. steam ; H_c = 1040.7 Btu/1b.
(*iii*) at 15 psia, enthalpy of sat. water ; H_d = 181.1 Btu/1b.
and specific volume of water at 15 psia = 0.01672 cft.]

(*i*) Work of expansion $= h_b - h_c = 1191.7 - 1040.7 = 151$ Btu/1b

$$\text{and (ii) Pump-work} \quad = v(P_1 - P_2) = \frac{0.01672 - (15130) \times 144}{778}$$

$$= -0.356 \text{ Btu/1b}$$

$\therefore$ Net-work $= 151 - 0.356 \approx 150.6$ Btu/1b
(Note that the work of compression is negiligble)

(iii) The heat absorbed at the high temperature,

$$\begin{aligned} Q_1 &= h_b - h_a \\ &= h_b - h_d + v(P_1 - P_2) \\ &= 1191.7 - 181.1 + (-0.356) \approx 1010.2 \text{ Btu/lb} \end{aligned}$$

$$\therefore \text{ efficiency, } \eta = W/Q_1 = \frac{150.6}{1010.2} = 0.149 \text{ ; } i.e. \text{ } 14.9 \text{ \%}$$

Internal Combustion Engines. In the internal combustion engines, heat is not supplied from outside. It is generated within the engines from the combustion of some suitable fuels. The common internal combustion engines used in automobiles are either *(i) Otto engines,* in which heat is absorbed at constant volume or *(ii) Diesel engines,* in which heat is absorbed at constant pressure. A brief outline of the operation of these two types of engines is given here.

4-9. The Otto Cycle

The Otto engine works in a typical four stroke cyclic process as shown in Fig. 4*g*. The engine consists of a cylinder with a frictionless piston and is provided with an intake and an exhaust valve. To start with, the piston is in the limiting position at the topdead centre (TDC), [Fig. 4*g*(*a*)].

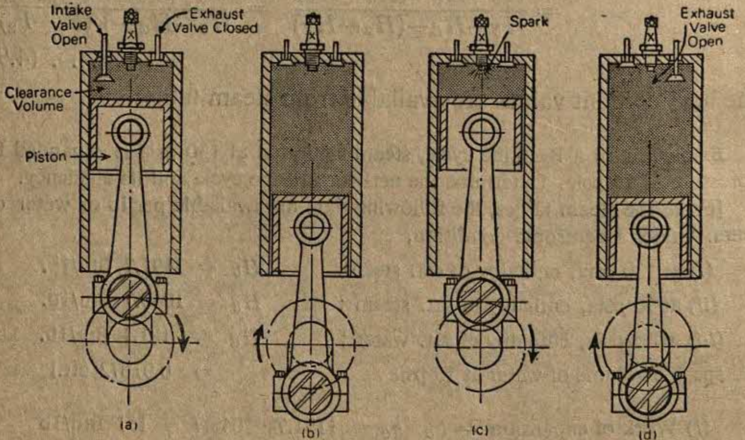


Fig 4*g*. The strokes of an Otto engine. (*a*) the piston at TDC (*b*) the piston at BDC after suction (*c*) power-stroke starts (*d*) exhaust stroke begins.

In the first intake stroke, air-fuel mixture flows, by suction, into the cylinder at constant pressure until the piston-head reaches the bottom-dead centre (BDC), Fig (*b*). In the second stroke the air-fuel mixture is compressed adiabatically by closing all the valves. In the next step, the mixture is ignited by means of a sparking plug (Fig *c*) hence it is called a *spark ignition* engine. The combustion produces a large amount of heat very rapidly, during which the volume practically remains constant. The pressure rises considerably. This is followed by the expansion of the high pressure high-temperature gas (Fig. *d*). This indeed is the work-producing step. During expansion work is used in turning a turbine (say). At the end of the expansion, when the piston-head reaches BDC, the exhaust valve is opened and the pressure falls to almost the initial state but the volume remains constant. Finally, during the exhaust the piston is pushed up to the TDC point. The cycle is complete.

These changes may be indicated with a *P-V* diagram as in Fig. 4*h*. OA denotes the initial intake of the air-fuel mixture at constant pressure. AB is the next *adiabatic compression* of the mixture when the pressure rises considerably. The mixture is then ignited by sparks, when heat Q_1 is evolved and absorbed by the gas at *constant volume*. The pressure-rise is indicated by BC. The vapours are then allowed to expand *adiabatically* along CD producing the work. Finally, the gas allowed to escape through the exhaust valve at constant volume.

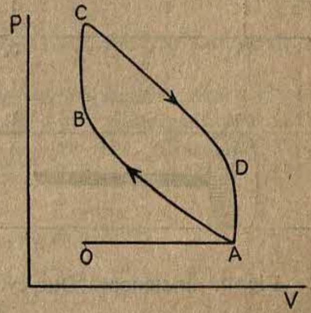


Fig. 4*h*

The Otto cycle thus consists of two adiabatic processes with two alternate constant-volume processes. The fluid is predominantly air mingled with some gasoline-like fuel required for the generation of heat. It is indeed a gas power cycle. To analyse such a cycle and to estimate its efficiency, it is convenient to regard it as an ideal cycle using only air as the working medium. Such an idealised cycle is called *air-standard Otto cycle*. It is aptly represented by the *P-V* indicator diagram in Fig. 4*i*. The efficiency of an air-standard Otto cycle may be computed as follows :

In fig. 4*i*, the adiabatic compression is denoted by *ab* and the adiabatic expansion producing work by *cd*. In the isochoric change *bc*, heat (Q_1) is produced. Along *da* the gas is reduced to its orignial pressure, when (Q_2) heat is given out by the system. The pressure, volume and temperatures at different stages are denoted by P, V and T with suffixes indicating different points. C_v is the heat capacity of the fluid at constant volume, supposed to remain constant.

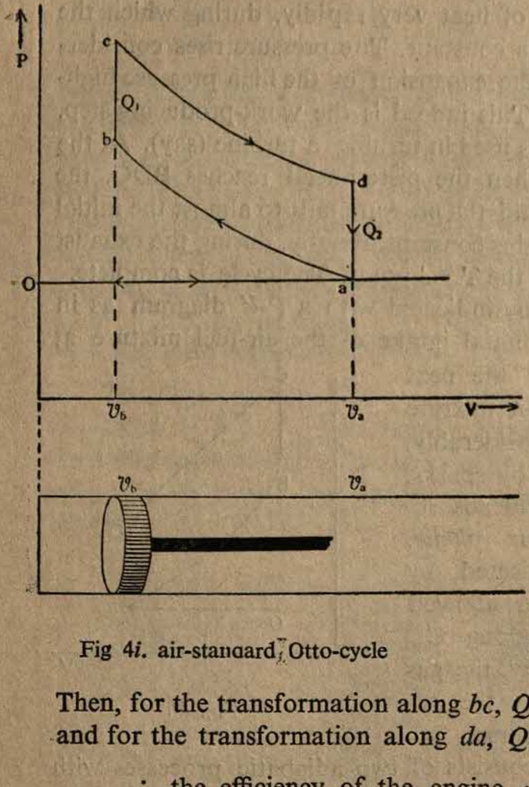


Fig 4*i*. air-standard Otto-cycle

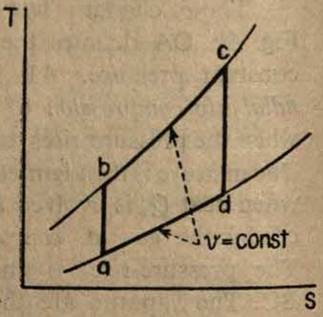


Fig 4*j*. air standard Ctto-cycle

Then, for the transformation along bc, $Q_1 = C_v(T_c - T_b)$
and for the transformation along da, $Q_2 = C_v(T_d - T_a)$

$$\therefore \text{ the efficiency of the engine, } \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$= 1 - \frac{T_d - T_a}{T_c - T_b} \quad \ldots (4.10)$$

Further we know :

$$T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1}, \text{ and } T_d V_a^{\gamma-1} = T_c V_b^{\gamma-1}, \ (\text{since } V_c = V_b)$$

$$\therefore \quad \frac{T_d}{T_a} = \frac{T_c}{T_b} \text{ or } \frac{T_d}{T_c} = \frac{T_a}{T_b} = \frac{T_d - T_a}{T_c - T_b}$$

Again, $\left(\frac{V_b}{V_a}\right)^{\gamma-1} = \frac{T_d}{T_c} = \frac{T_d - T_a}{T_c - T_b}$

$$\text{Hence efficiency, } \eta = 1 - \frac{T_d - T_a}{T_c - T_b} = 1 - \left(\frac{V_b}{V_a}\right)^{\gamma-1} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad \ldots (4.11)$$

where ρ is called the compression ratio; it is the ratio of the volumes at the beginning and at the end of the compression step, *i.e.*, $\rho = V_a/V_b$.

It is evident that the efficiency of an Otto cycle increases with increase in the compression ratio, ρ. The value of γ is taken as 1.4 (Fig. 4*k*). The rate of increase in efficiency slows down at higher compression. The results in actual tests with internal combustion engines show a lower efficiency than those calculated. This is due to non-ideal condition and especially for using a constant value for γ. The value of γ changes appreciably with the variation of temperature in the different stages of the cycle.

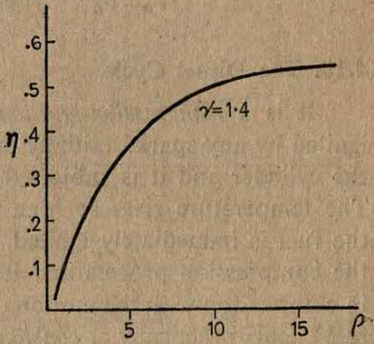


Fig 4*k*. Efficiency of Otto-cycle

Example : The compression ratio of an Otto engine working with 1 lb of air is 8 : 1. The pressure and temperature at the start of the compression are 15 psia and 60°F. The highest pressure attained is 1600 psia. Determine the efficiency and mean effective pressure of the cycle. C_v for 1 lb of air = 0.171 Btu/°F.

Consider $P-V$ diagram of the Otto cycle in fig 4*i*.

Given : $\rho = 8.0$, $T_a = 60 + 460 = 520\text{R}$, $P_a = 15$ psia

$\gamma = 1.4$, $C_v = 0.171$ Btu/°F

$$\therefore \text{ Efficiency } \eta = 1 - \left(\frac{1}{8}\right)^{\gamma-1} = 1 - \frac{1}{(8)^{0.4}} = 0.56$$

$$\text{Again } T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1}; \text{ or } T_b = T_a \left(\frac{V_a}{V_b}\right)^{\gamma-1} = 520(8)^{1.4-1} = 1196°\text{R}$$

$$\text{And} \quad P_b V_b^{\gamma} = P_a V_a^{\gamma}\ ; \text{ or } P_b = P_a \left(\frac{V_a}{V_b}\right)^{\gamma} = 15\ (8)^{1.4} = 276 \text{ psia}$$

$$V_a = \frac{RT_a}{P_a} = \frac{53.3 \times 520}{144 \times 15} = 12.65 \text{ ft}^3$$

$$\text{Also} \quad T_c = \frac{P_c \times T_b}{P_b} = \frac{1600 \times 1196}{276} = 6933°\text{R, (since } V_c = V_b)$$

$$V_b = \frac{V_a}{\rho} = \frac{12.65}{8} = 1.58 \text{ ft}^3$$

i.e., volume change in compression = 12.65 − 1.58 = 11.07 ft³

Heat absorbed per cycle, $Q_1 = C_v(T_c - T_b) = 0.171(6933-1196) = 981$ Btu

$$\therefore \quad \text{mean effective pressure, } mep = \frac{\text{work produced per cycle}}{\text{volume change in compression}}$$

$$\text{or} \quad mep = \frac{\eta Q_1}{V_a - V_b} = \frac{8 \times 981 \times 778}{11.07 \times 144} = 268 \text{ psia}$$

4.10. The Diesel Cycle

It is a *compression-ignition* engine in which the fuel is not ignited by any spark. Initially on intake only air is introduced into the cylinder and it is subjected to high compression adiabatically. The temperature rises so high that when fuel is sprayed into it, the fuel is immediately ignited. The fuel is rejected at the end of the compression process and it is added in such a regulated rate in comparison with the motion of the piston that combustion of the fuel occurs practically at *constant pressure*. The heat of combustion is taken up by the gas with a considerable rise in temperature. The gas mixture is then adiabatically expanded when the temperature falls and it is the work-producing step. Finally, by opening an exhaust value, the gas is reduced to the orignial temperature and pressure ; the cycle is completed.

Analogous to the Otto cycle, an air-standard Diesel cycle may be idealised as in the *P-V* diagram (Fig 4*l*). The four steps of this cycle are : (*i*) adiabatic compression *ab*, (*ii*) combustion of

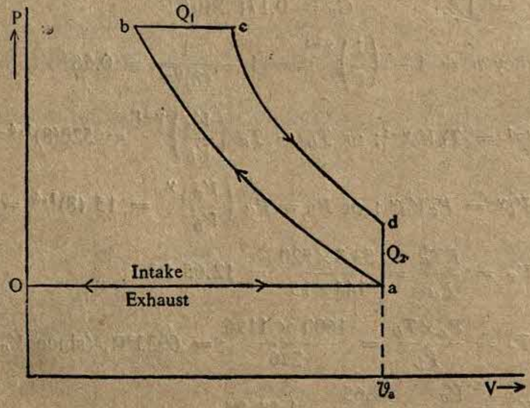


Fig. 4*l*
The air-standard Diesel cycle

fuel *i.e.*, heat absorption Q_1 at constant pressure *bc* (*iii*) adiabatic expansion *cd* (*iv*) constant volume process in exhaust, *da*, Q, heat released.

A *T-S* diagram is also given in Fig 4*m*.

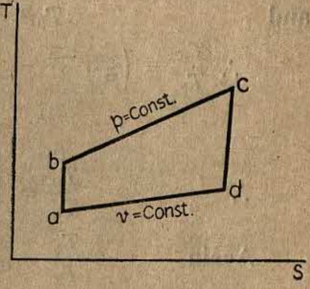


Fig. 4*m*.

The efficiency of the air-standard diesel cycle may be easily computed.

For the isobaric change *bc*,

$$Q_1 = C_p(T_c - T_b)$$

For the isochoric change *da*,

$$Q_2 = C_v(T_d - T_a)$$

The efficiency of the engine,

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_v}{C_p} \cdot \frac{T_d - T_a}{T_c - T_b} = 1 - \frac{1}{\gamma} \cdot \frac{T_d - T_a}{T_c - T_b} \quad \ldots (4.12)$$

The heat is rejected along *da* at constant volume. Instead we might allow the adiabatic expansion to proceed until it reaches the point *e*, when pressure becomes the original external pressure and the temperature T_e. The gas then at constant pressure be cooled to volume V_a at *a* (Fig. 4*n*), the heat rejected $Q_2 = C_p(T_e - T_a)$.

The change *da*, is then sum of the changes, *de* and *ea*. The Diesel cycle *abcd* is thus transformed into the cycle *abce*. The efficiency, then,

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_p(T_e - T_a)}{C_p(T_c - T_b)} = 1 - \frac{T_e - T_a}{T_c - T_b} \quad \ldots (4.13)$$

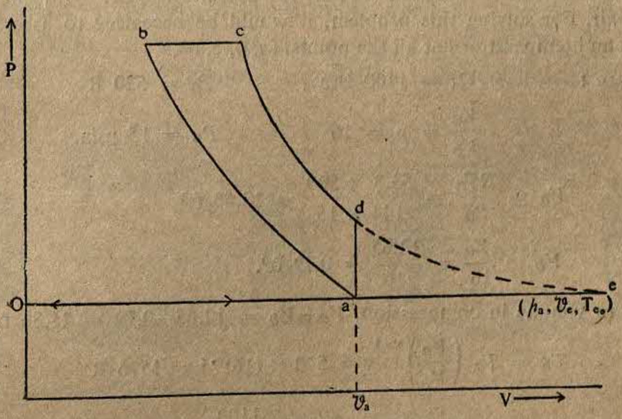


Fig. 4*n*. The Diesel Cycle (modified)

But we know : $$T_cP_e^{\frac{1-\gamma}{\gamma}} = T_eP_a^{\frac{1-\gamma}{\gamma}}$$

and $$T_bP_c^{\frac{1-\gamma}{\gamma}} = T_aP_a^{\frac{1-\gamma}{\gamma}} \quad [\because P_b = P_c]$$

$$\therefore \frac{T_c}{T_e} = \left(\frac{P_a}{P_c}\right)^{\frac{1-\gamma}{\gamma}} = \left[\left(\frac{V_c}{V_a}\right)^{\gamma}\right]^{\frac{1-\gamma}{\gamma}} = \left(\frac{V_c}{V_a}\right)^{1-\gamma} = \left(\frac{V_c}{V_d}\right)^{1-\gamma}$$

$$= \left(\frac{1}{\rho}\right)^{1-\gamma}$$

$$\therefore \quad \frac{T_e}{T_c} = \left(\frac{1}{\rho}\right)^{\gamma-1}$$

Again $$\frac{T_b}{T_a} = \left(\frac{P_a}{P_c}\right)^{\frac{1-\gamma}{\gamma}}$$

Hence $$\frac{T_e}{T_c} = \frac{T_a}{T_b} = \frac{T_e-T_a}{T_c-T_b}$$

The efficiency, $$\eta = 1 - \frac{T_e-T_a}{T_c-T_b} = 1 - \frac{T_e}{T_c} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad \ldots (4.14)$$

(*cf.* Carnot cycle and Otto cycle).

The *compression ratio* ρ is much larger in the Diesel engine than that in the Otto engine. This explains the higher efficiency of the former.

Example : The pressure and temperature at the beginning of a diesel cycle are 15 psia and 60°F. Its compression ratio is 16 : 1 and the heat supplied by combustion is 1100 Btu/1b. Calculate its efficiency and mep, assuming air-standard condition, $[\gamma = 1.4, \ C_p = 0.24$ Btu/lb-°F]

Consider the P-V diagram (Fig 4*l*) for the diesel cycle. With one pound mass of air. For solving this problem, it would be necessary to ascertain the volumes and temperatures at all the points, (a, b, c, d).

Given : $Q_1 = 1100$ Btu $\qquad T_a = 520$ R

$$\frac{V_a}{V_b} = \rho = 16 \qquad P_a = 15 \text{ psia.}$$

$$\therefore \quad V_a = \frac{RT_a}{P_a} = \frac{53.3 \times 500}{144 \times 15} = 12.65 \text{ ft}^3$$

$$V_b = \frac{V_a}{16} = \frac{12.65}{16} = 0.79 \text{ ft}^3.$$

Change in volume in compression, $V_a - V_b = 12.65 - 0.79 = 11.86$ ft³

Again, $$T_b = T_a\left(\frac{V_a}{V_b}\right)^{\gamma-1} = 520 \times (16)^{0.4} = 1576 \text{ R}$$

$$T_c = T_b + Q_1/C_p = 1576 + \frac{1100}{0.24} = 6160 \text{ R}$$

Further, $V_b = V_a/16 = V_d/16$

and $\quad V_c = V_b \dfrac{T_c}{T_b} = \dfrac{6160}{1576} V_b = 3.89\ V_b = 3.89 . \dfrac{V_d}{16} = \dfrac{V_d}{4.11}$

or $\quad \dfrac{V_c}{V_d} = \dfrac{1}{4.11}$

$$\therefore \quad T_d = T_c \left(\frac{V_c}{V_d}\right)^{\gamma-1} = 6160 \left(\frac{1}{4.11}\right)^{0.4} = 3500°\text{R}$$

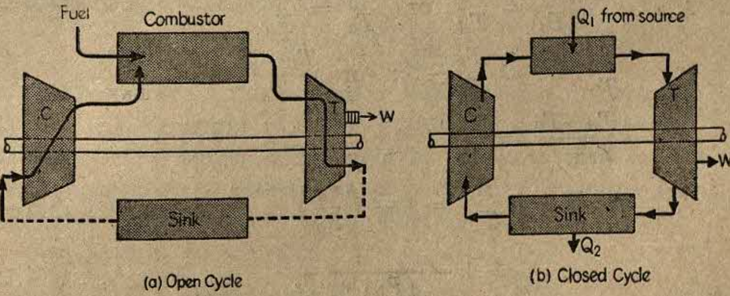
$$\text{The efficiency, } \eta = 1 - \frac{T_d - T_a}{\gamma(T_c - T_b)} = 1 - \frac{3500 - 5200}{1{\cdot}4\,(6160 - 1576)} = 0.54$$

$$mep = \frac{\omega}{v_a - v_b} = \frac{\eta Q_1}{v_a - v_b} = \frac{.54 \times 1100 \times 778}{144 \times 11.86} = 270.6 \text{ psia}$$

4-41. The Brayton Cycle

The operation of the gas turbine power plants is basically dependent on the Brayton cycle. The initial intake is the atmospheric air which is compressed sufficiently to reach a high pressure and temperature. Fuel is then injected for combustion in the compressed air and heat is absorbed at *constant pressure*. The hot gases are then allowed to expand and cool in turning the turbine (producing work for the generator). This expansion continues almost to the initial low pressure. The gas is then allowed to escape to the atmosphere. Heat rejection is achieved by cooling in the atmosphere. Fresh intake of air then ensues. This is the *open cycle* [Fig 4o(*a*)].

To analyse and to estimate its performance theoretically the usual practice is to regard the Brayton cycle as a *closed one* using air (or helium or argon) as the working medium. In the closed cycle, the air is in continuous circulation. After compression, heat



(a) Open Cycle (b) Closed Cycle

Fig 4o. The Brayton cycle

is supplied to the cycle by burning some cheap or low-grade fuel externally. As usual the work is produced in the turbine during expansion to the original low-pressure. The cycle is completed by transfer of residual heat to the surroundings through a heat-exchanger [Fig 4*o*(*b*)].

The closed Brayton cycle is thus an air-standard one. It consists of two adiabatic steps alternating with two *constant pressure* processes. These are shown in Fig 4*p* in *P-V* and *T-S* diagrams.

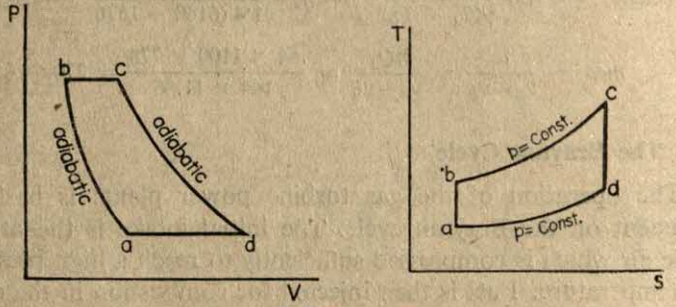


Fig. 4*p*. The Brayton cycle (air-standard)

The efficiency may be determined as follows:

For the isobaric process *bc*, $Q_1 = C_p(T_c - T_b)$

For the isobaric process *da*, $Q_2 = C_p(T_d - T_a)$

$$\therefore \text{ Efficiency, } \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_d - T_a}{T_c - T_b}$$

For the adiabatic processes $\dfrac{T_b}{T_a} = \left(\dfrac{P_b}{P_a}\right)^{(\gamma-1)/\gamma}$ . . . (*i*)

and $\dfrac{T_c}{T_d} = \left(\dfrac{P_c}{P_d}\right)^{(\gamma-1)/\gamma} = \left(\dfrac{P_b}{P_a}\right)^{(\gamma-1)/\gamma}$, (since $P_c = P_b$ and $P_d = P_a$)

$$\therefore \quad \frac{T_b}{T_a} = \frac{T_c}{T_d} \text{ or } \frac{T_d}{T_a} = \frac{T_c}{T_b}$$

$$\text{or} \quad \frac{T_d}{T_a} - 1 = \frac{T_c}{T_b} - 1 \; ; \text{ or } \frac{T_d - T_a}{T_a} = \frac{T_c - T_b}{T_b}$$

$$\text{or} \quad \frac{T_d - T_a}{T_c - T_b} = \frac{T_a}{T_b}$$

$$\therefore \quad \eta = 1 - \frac{T_a}{T_b} = 1 - \left(\frac{P_a}{P_b}\right)^{(\gamma-1)/\gamma} \quad [\text{ from } (i) \text{ above}]$$

$$= 1 - \frac{1}{\left(\dfrac{P_b}{P_a}\right)^{(\gamma-1)/\gamma}} \qquad \text{. . . (4.15)}$$

The efficiency is dependent on the initial and final pressure in the compression process. Using air ($\gamma = 1.4$) and a compression pressure ratio ($P_b/P_a = 10$), the calculated efficiency is nearly 40%.

4.12. Refrigeration Cycles

A. The Reversed Carnot Cycle. If the operation of the Carnot cycle be carried out in a reverse direction, then heat (Q') will be taken up by the engine from the colder body (sink) and a larger amount of heat (Q) will be delivered to the hotter body. This would not violate the second law but this would require an input of work. In consequence, the cold body becomes still colder. The engine operating in such a cycle is called a *refrigerator*.

Refrigeration cycle is most commonly used in preservation of foods (frigidaires), in manufacturing ice ; in air-conditioning of rooms. Besides, it has now many important commercial applications as in oil-refinery process, in treatment of special steel, in making 'cold rubber', and in various other fields. There is now a special field of investigation for low temperature production, called *cryogenics*.

The ideal refrigeration cycle would be the reversed Carnot's cycle, as represented in fig. 4*q*. It consists of (*i*) two isothermal processes in which heat Q_2 is absorbed at the lower temperature T_2 and the heat Q_1 is given up at the higher temperature T_1 and (*ii*) two adiabatic processes. Suppose network required for the transfer is W. Then, in the reversible cycle,

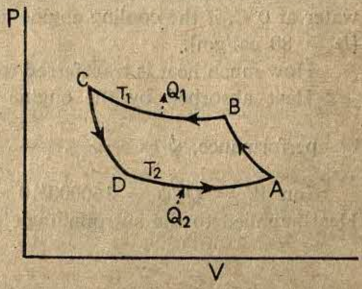


Fig. 4*q*. Reversed Carnot cycle

$$W = Q_1 - Q_2$$

Obiviously, the larger the amount of heat removed from the colder body by a given input of work, better is the refrigeration. The success of refrigeration is expressed by what is called *coefficient of performance* (*cop*). The *cop* is defined by the quantity of heat removed by unit amount of work. That is,

coefficient of performance,

$$\psi = \frac{\text{heat removed}}{\text{work input}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

In a Carnot's cycle, $$\frac{Q_2}{Q_1-Q_2} = \frac{T_2}{T_1-T_2}$$

$$\therefore \quad cop,\ \psi = \frac{T_2}{T_1-T_2} \qquad \ldots (4.16)$$

$$\text{Also } W = Q_2/\psi = Q_2 \cdot \frac{T_1-T_2}{T_2} \qquad \ldots (4.17)$$

Heat-Pump. Sometimes the reversed cycle is used to supply heat to the higher temperature. For example, in winter a room is to be supplied heat to maintain normal temperature by drawing heat from the outside cold air or a lake. Literally, heat is pumped into the room by cooling the cold lake. When the objective is to supply heat to the higher temperature, the refrigerator serves as a *heat-pump*. More heat delivered to the higher temperature with a given input of work better is the heat-pump. Its coefficient of performance,

$$cop_{\text{heat-pump}} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2} \qquad \ldots (4.18)$$

Example. Calculate the least work needed to produce 2 Kg. of ice from water at 0°C, if the cooling engine gives up heat to the surroundings at 27.3°C [l_f = 80 cal/gm].

How much heat is transferred to the surroundings for the process?

Heat absorbed by the engine at 273°K, $Q_2 = 2000 \times 80 = 160000$ cal

performance, $\psi = \frac{T'}{T-T'} = \frac{273}{27.3} = 10$

But $W = Q_2/\psi = 160000/10 = 16000$ cal $= 67.2$ kj

[Heat supplied to the surroundings, $Q_1 = Q_2 + W$
$= 160000 + 16000 = 176000$ cal

Example. A heat-pump is used to supply heat to a room at 27°C by extracting the same from cold air outside at 7°C. What amount of work would be needed to supply each kilocalorie of heat to the room?

For the heat pump, (*Cop*) $\psi = \frac{T}{T-T'} = \frac{300}{20} = 15$

Now $W = Q_1/\psi = \frac{1000}{15} \times 4.2 \times 10^{-3}$ kj $= 0.28$ kj.

Note : From eqn. (4.17), $W = Q_2 \frac{T_1-T_2}{T_2}$, it is evident that the minimum work (w) required to remove a definite quantity of heat (Q_2) in refrigeration increases as the lower temp. (T_2) is decreased. If T_2 is lowered to 0°K, then infinite amount of work would be needed. That is, the refrigeration would not be possible.

Unit of Refrigeration. The capacity of refrigeration is expressed in terms of **tons** of refrigeration. A 1-*ton* refrigerator extracts in a day an amount of heat just enough to freeze one ton of water at 32°F.

Now 1 short ton = 2000 lb, latent heat of fusion = 144 Btu/lb

$\therefore$ Heat extracted in one day is $144 \times 2000 = 288000$ Btu/day

or heat extracted $Q_2 = 288000/(24 \times 60) = 200$ Btu/min.

Hence a 5-ton refrigerator would make $5(200) = 1000$ Btu of refrigeration per minute.

Suppose a y-horsepower motor supplies the needed work to a x-ton refrigerator. That is,

the heat removed per min, $Q_2 = x \times 200$ Btu

and the work done per min, $w = y \times 42.4$ Btu

$\therefore$ cop of the refrigerator, $\psi = \dfrac{Q_2}{w} = \dfrac{x \times 200}{y \times 42.4} = 4{\cdot}72\,\dfrac{x}{y}$

The practical realisation of a reversible Carnot refrigeration cycle is difficult. The heat-transfer between the working gas and the surroundings under *isothermal conditions* is quite difficult. The heat-transfer becomes easier if a liquid is allowed to vaporise withdrawing latent-heat from the surroundings or vice-versa. This is why in most practical and commercial refrigeration cycles, the working medium of the engine is liquid-vapour.

B. Vapour Compression Refrigeration

For a good performance, the heat transfer processes in the refrigeration system should be at constant temperatures. This can be achieved to a large extent by using a vapour compression cycle for refrigeration. The working fluid may be in the liquid and in the vapour phase. The outline of the process is schematically shown in Fig. 4*r*(*a*).

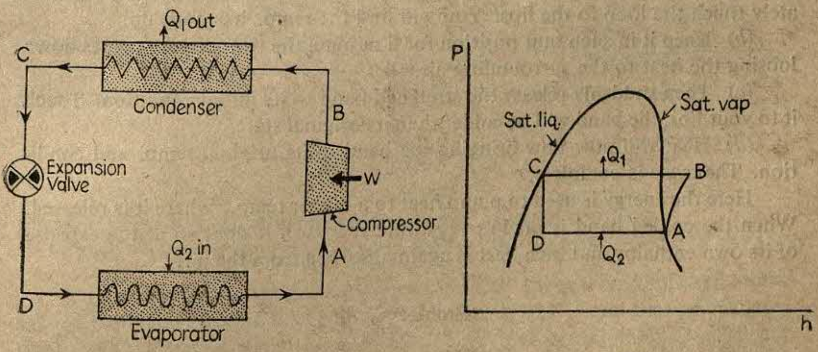


Fig. 4*r*. (*a*) Vap. Compression Refrigeration system

(*b*) p-h diagram

The saturated vapour (say, ammonia or freon) is taken in state A and then compressed adiabatically at a higher pressure and temperature to a super-heated vapour as at state B. The vapours are then led through a coil immersed in the coolant at constant pressure. The vapour gives up heat Q_1 to the coolant at temp T_1 and is condensed to the liquid state at C. For returning to the low-pressure, the liquid is adiabatically led through an expansion value. The outcoming liquid at a low-pressure and temperature is made to pass through the evaporator at constant pressure. The liquid here absorbs heat Q_2 from the surrounding cold-temperature environment and turns into the saturated vapour as at A. The cycle is complete. The heat is removed from the low-temp. bath of the evaporator and is delivered to the higher-temperature bath of the coolant.

The cycle may be analysed with a pressure-enthalpy diagram as in fig 4*r*(*b*). *P-V* diagram would not help as the fluid would be in liquid state in some stages of the cycle. Here

$$Q_2 = h_A - h_D = h_A - h_C \quad , \text{ (CD being an adiabatic change)}$$

$$Q_1 = h_B - h_C$$

$$W = Q_1 - Q_2 = (h_B - h_C) - (h_A - h_C) = h_B - h_A$$

$$\therefore\ cop\ ,\ \psi = \frac{Q_2}{Q_1 - Q_2} = \frac{h_A - h_C}{h_B - h_A}$$

A very ingeneous and interesting experiment has been suggested to imitate such cycles (Calingáert. J. chem. Edn. 1962, 29, 405). Take an ordinary rubber band loop about 2 mm wide and 12 cm circumference. If you touch this loop with your lips, the temp. is the same as that of the room. Now,

(*a*) Stretch this band suddenly to three or four times its length and immediately touch the loop to the lips. You will find the temp. has gone up.

(*b*) Keep it in such taut position for a minute, the temperature comes down loosing the heat to the surrounding air.

(*c*) Then suddenly release the stretched band to its initial condition. Touch it to your lips, the band will be colder than its original state.

(*d*) Heat will now flow bringing the band to its original temp. and condition. The cycle is complete.

Here the energy is used to pump heat to a higher temp., where it is released. When the cooled band is made to restitute the work it does so at the expense of its own enthalpy and then heat is again absorbed from the air.

Problems

1. Liquid oxygen boils at 90°K and liquid hydrogen at 20°K. What is the efficiency of a reversible engine working between heat reservoirs at these two

tmeperatures? If the same efficiency be required for an engine with a cold reservoir at 27°C, what must be the temp. of the source?

Ans. $\eta = 0.77$, $T = 1077°\text{C}$.

2. In the furnace of a large steam engine 6×10^5 Kcal/hour heat is evolved. The efficiency of the engine is 35%. What electrical power will be obtained from a dynamo driven by this steam if the efficiency of the dynamo be 95%. The furnace supplies heat at 297°C and the cooling water escapes at 57°C.

Ans. 84000 Kcal/hr.

3. A Carnot refrigerator works between 0°C and 100°C. If 1000 joules are absorbed from the low temperature bath, how many calories are carried to the high temperature reservoir? Calculate the coefficient of performance.

Ans. $\psi = 2.73$, $Q_1 = 325.2$ cal.

4. A Carnot engine converts $\frac{1}{6}$ of the heat supplied into work. If the temperature of the sink be reduced by 62°C, the efficiency of the engine is doubled. Find out the temperatures of the source and the sink.

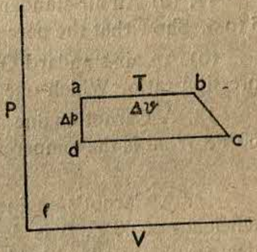
Ans. $T_1 = 372°\text{K}$, $T_2 = 310°\text{K}$.

5. In order to increase the efficiency of a Carnot engine, would you increase T keeping T' constant, or decerase T' keeping T constant?

6. One mole of a perfect gas ($C_p = 7$ cal/mole) working in a Carnot engine between 1000°K, and 400°K does work of 1000 cal during isothermal expansion at 1000°K. What would be net work available per cycle of operation? Calculate the work done on the gas and the increment in enthalpy during adiabatic compression.

Ans. net work, $w = 600$ cal, $w_4 = 3000$ cal, $\Delta H_4 = 4200$ cal.

7. A liquid in contact with its vapour is enclosed in a cylinder with a piston at temp. T. The following reversible Carnot Cycle is then carried out. (*a*) 1 gm of liquid is vaporised reversibly isothermally at constant pressure P. (*b*) This vapour (1 gm) is separated and made to undergo adiabatic expansion when the temp. falls to T', ($T' = T - \Delta T$). The vapour is next isothermally condensed till whole of it is liquefied and finally compressed to its initial state adiabatically and added to the cylinder.



$$\text{Show that } \frac{\partial P}{\partial T} = \frac{l}{T\Delta v}$$

Where l = latent heat of vaporisation per gm, assumed constant.

[Note : work of the cycle = area abcd of the diagram = $\Delta P \times \Delta v$]

8. A nuclear power plant is planned for 8×10^5 kw and is established on the side of Nermada river (sink). The reactor temp. is 323°C and that of the river water 25°C. What is the maximum efficiency? The actual thermal efficiency is 80% of the maximum, how much heat would be discarded into the river? What would be the rise in temp. of river-water if its flow-rate be 10^5 litre/sec.

The maximum efficiency, $\eta_{max} = 1 - \frac{596}{298} = 0.5$

The real efficiency, $\eta = 0.8(0.5) = 0.4$

$\therefore$ The energy produced in the reactor, $Q_1 = \frac{w}{\eta} = \frac{8 \times 10^5}{0.4}$

$= 2 \times 10^6$ Kw $= 2 \times 10^9$ j/sec.

$\therefore$ heat discharged in the river, $Q_2 = 2 \times 10^6 - 8 \times 10^5 = 1.2 \times 10^6$ Kw

$= 2.86 \times 10^8$ cal/sec.

If ΔT be the rise in temperature, then

$$\Delta T = \frac{Q_2}{m \times C_p} = \frac{2.86 \times 10^8}{(10^5 \times 10^3) \times 1.0} = 2.86°\text{C}$$

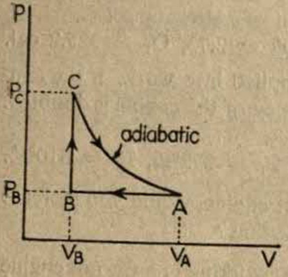


Fig. 4s

9. A three-step ideal-gas cycle is represented in Fig 4s. Show that the thermal efficiency

$$\eta = 1 - \gamma \cdot \frac{(V_A/V_B) - 1}{(P_c/P_B) - 1}$$

10. A three-step reversible cycle consists of (*i*) an isothermal expansion at T_1, (*ii*) constant-volume cooling to T_2 and (*iii*) an adiabatic compression to the initial state. Calculate the work per cycle using 1 mole of an ideal-gas.

Show that its efficiency, $\eta = 1 - \frac{T_1 - T_2}{T_1 \, ln(T_1/T_2)}$

11. (*a*) An air-standard Otto-cycle has its compression ratio raised from 5 to 6. Show that the percentage increase in its efficiency is about 8%.

(b) An air-standard Otto-cycle and a diesel cycle both have the same compression ratio. Which one will have a higher efficiency?

12. A Carnot engine develops 3 hp and rejects 9000 Btu/hr to the sink at 60°F. What is the temperature of the source? (1 hp = 42.4 Btu/min)

Ans. 501°F

13. A Carnot's engine whose low temperature reservoir is at 12°C has an efficiency of 40%. It is desired to increase the efficiency to 60%. By how many degrees centigrade should the temp. of the reservoir at the nigher temperature be increased? (C.U. Phy. Hons. 1964) **Ans.** 237.5.

14. What is the best efficiency of a refrigerator working between 20°C and −10°C? What minimum work has to be done to enable it to withdraw 1000 cal from −10°C and reject the heat to the surroundings at 20°C ?

Ans. $\psi = 8.8, w = 114$ cal.

15. A heat pump is used to supply heat to a room at 27°C by extracting the same from cold air outside at 7°C. What amount of work would be necessary for supply of each kilocalorie of heat to the room? **Ans.** 277.2 joules.

16. A heat pump is used to maintain the temp. of a building at 80°F, when atmospheric temp. is 10°F. Heat losses from the building is 69400 Btu per hour. The heat pump efficiency is 45 percent. What is the actual coefficient of performance of the heat-pump? If electricity sells at 10 paise per kw-hour, what is the cost involved per hour? [1 kw-hr. = 3412 Btu/hr.]

Ans. $\psi = 3.47$, Cost = 59 paise.

17. A Carnot engine is supplied 500 cal/cycle from the source and it operates between 727 and 27°C. Sixty per cent of the work output is used in running a heat pump which removes 1050 cal/cycle from the low-temperature lake and rejects the same to the surroundings at 27°C. Find the temp. of the lake.

Ans. −23°C.

18. (*i*) Determine the cop of a heat-pump operating between 20 and 80°F which has a power input of 4 hp.

(*ii*) The thermal efficiency of a Carnot engine is $\frac{1}{4}$. Calculate the *Cop* of (*a*) Carnot refrigerator (*b*) a Carnot heat-pump.

19. A refrigerator is operated between −10°F and + 81°F to produce 8 tons of refrigeration. Calculate the power required to operate the refrigeration plant.

Ans. 7.95 hp.

20. A Carnot refrigerator removes heat from a sink at 440°R and rejects the same to the atmosphere at 510°R. The refrigerator is powered by a Carnot engine receiving heat from a source at 1530°R and rejecting to the atmosphere. Determine the ratio of the heat supplied to the engine and the heat removed by the refrigerator.

Ans. 0.24.

21. An air-standard Otto-cycle has a compression ratio 8.5. The pressure and temperature at the start of the compression are 14·5 psia and 550°R. The pressure is trebled during the heat-addition step. (*i*) What is the efficiency of the cycle ? (*ii*) What would have been the efficiency of the Carnot engine working between the same temperature limits ?

Ans. (*i*) 0.52, (*ii*) 0.85.

22. An air-standard diesel cycle has $\rho = 15$. At the start of the compression, the pressure and temperature are 15 psia and 420°R. The maximum temp. of the cycle is 4200°R. Find out the thermal efficiency and *mep*.

Ans. (*i*) 0.5, (*ii*) 177 psi.

23. A hotel at Simla is maintained at a constant temp. of 77°F, when outside temp. is 23°F, by a heat-pump with a 60% efficiency. The heat loss is 68240 Btu/hr. Calculate

(*i*) the true coefficient of performance of the heat pump

(*ii*) Cost per day of electricity bill at the rate of 20 paise per kw-hour. [1 kw-hour = 3412 Btu-hr]

Ans. (*i*) 5.96, (*ii*) Rs. 16.10.

CHAPTER 5

ENTROPY

A better approach to the understanding of the Second Law is possible through the introduction of a new thermodynamic function, called *entropy*. We shall first attempt to follow the steps which lead us to the concept of this function.

5.1. δq is not a perfect differential but δq/T is a perfect differential

We have seen in Sec. 1.8, that the amount of heat δq absorbed or evolved during the change of a system from one given state to another given state depends on the way the change of the system is carried out, *i.e.*, δq depends on the path of the transformation. Therefore δq cannot be a perfect differential. To illustrate ; (small thermal change is δq and not dq).

(*i*) Suppose a quantity of a perfect gas (say 1 mol) undergoes a *reversible* expansion from volume V_1 to V_2 when the temperature changes from T_1 to T_2. From the First law,

$$\delta q = dU + PdV$$

$$\text{or} \quad \int_{I}^{II} \delta q = \int_{I}^{II} dU + \int_{I}^{II} PdV$$

$$= \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} RTd\ln V \qquad \ldots (5.1)$$

$$\text{or} \quad \int_{I}^{II} \delta q = C_V(T_2 - T_1) + \int_{V_1}^{V_2} RTd\ln V$$

The integral on the right-hand side, $\int_{V_1}^{V_2} RTd\ln V$ cannot be evaluated unless we know the relation between T and V. If T be constant (*i.e.*, isothermal change), the integral will have one value, and if T changes during the process, the integral will have different values. Thus the magnitude of $\int_{I}^{II} \delta q$ depends on the way the expansion is carried out.

Now, dividing the equation (5.1) by T, we have

$$\int_{I}^{II} \frac{\delta q}{T} = \int_{T_1}^{T_2} C_V \frac{dT}{T} + \int_{V_1}^{V_2} R d \ln V = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

That is, $\int \frac{\delta q}{T}$ for a given change from state I to state II can be evaluated without any reference to the path of the transformation. Hence $\int \frac{\delta q}{T}$ is independent of the way the change is carried out, though $\int \delta q$ is not. It is to be remembered that the heat-change δq takes place in a reversible way.

(*ii*) We can also arrive at this conclusion in other ways. Consider a Carnot cycle as represented in Fig. 5*a* in which *ab* and *cd* are the isothermals at temperatures T_1 and T_2; *bc* and *da* are the adiabatic stages. Let δq_1 be the heat supplied to the working system at T_1 and δq_2 be the heat rejected by it to the sink at T_2. All steps are *reversible*. We know, in a Carnot cycle,

$$\frac{\delta q_1 - \delta q_2}{\delta q_1} = \frac{T_1 - T_2}{T_1} \text{ or } \frac{\delta q_1}{T_1} = \frac{\delta q_2}{T_2}$$

(δq_2 is negative as it is rejected by the system.)

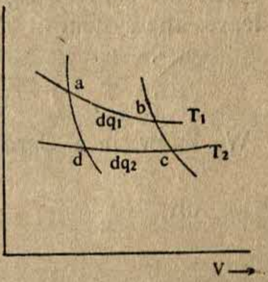


Fig. 5*a*
The Carnot's cycle

Now let us confine our attention to the change of the system from the point *a* to the point *c* and attempt to find out the ratio of the heat-change to the temperature at which the thermal change occurs. We can proceed from *a* to *c* either along *abc* or along *adc*.

Along the path *abc*, we have the isothermal *ab*, when heat-change δq_1 takes place at T_1, followed by adiabatic change *bc* having no heat-change. Hence,

$$\frac{\text{heat-change}}{\text{temp.}} = \frac{\delta q_1}{T_1} + 0 = \frac{\delta q_1}{T_1}$$

Along the path *adc*, the adiabatic *ad* involves no thermal change, but along the isothermal *dc*, remembering reversibility, heat absorbed would be δq_2 at temperature T_2. Hence,

$$\frac{\text{heat-change}}{\text{temp.}} = 0 + \frac{\delta q_2}{T_2} = \frac{\delta q_2}{T_2}$$

But
$$\frac{\delta q_1}{T_1} = \frac{\delta q_2}{T_2}$$

That is, the ratio of the heat-change to temperature, $\delta q/T$ is the same whatever path might be followed by the system in its *reversible* change. Hence, $\delta q/T$ is a perfect differential.

This reminds us of the First Law, $\triangle U = q - w$, where we found that however q and w might vary individually, the difference $(q-w)$ is a constant for a *given* change of a system. This constancy is the basis of the First Law and leads to the definition of *energy*, a state function. Likewise, for a *given* change, however q_r and T may very individually, the quotient q_r/T is a constant. This constancy, we shall see, is the basis of the Second law.

Moreover, if we consider the four steps of the entire Carnot cycle, the sum of $\delta q/T$-values would be (remembering dq_2 heat leaves the system at T_2),

$$\sum \frac{\delta q}{T} = \frac{\delta q_1}{T_1} + 0 - \frac{\delta q_2}{T_2} + 0 = \frac{\delta q_1}{T_1} - \frac{\delta q_2}{T_2}$$

We know, in a Carnot cycle, $\frac{\delta q_1}{T_1} = \frac{\delta q_2}{T_2}$, hence $\sum \frac{\delta q}{T} = 0$

or,
$$\oint \frac{\delta q}{T} = 0 \qquad \ldots (5.2)$$

5.2. Definition of Entropy

It is then obvious that the system has a thermodynamic function whose change, measured by $\frac{\delta q_{\text{rev}}}{T}$, is independent of the path of transformation of the system. Such a function should be a state function. This function has been called **entropy** by Clausius and is denoted by the symbol, S. Its change (dS) is measured by the ratio of the heat-change and the temperature at which the heat-change occurs, *i.e.*,

$$dS = \frac{\delta q_r}{T}, \quad \text{(the subscript } r \text{ indicates reversibility)}$$

If the heat-change occurs at different temperatures, then

$$dS = \frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2} + \frac{\delta q_3}{T_3} + \ldots = \Sigma \frac{\delta q_r}{T}$$

or $\int dS = \int \frac{\delta q_r}{T}$

We can then say :

(*i*) *Entropy S is a thermodynamic function, whose magnitude depends only on the parameters of the system (like U or H). S is thus independent of the past history of the system and can be expressed in terms of thermodynamic parameters (P, V, T).*

(*ii*) *The entropy-change dS is a perfect differential. Its value depends only on the initial and final states of the system, independent of the path of the change.*

(*iii*) *The entropy-change is measured by the reversible heat-change of the system divided by the temperature in absolute scale, i.e., $dS = \delta q_{rev}/T$.*

  (*a*) *when heat is absorbed by the system, δq is positive. T is always positive. Therefore, entropy-change dS is positive. Absorption of heat increases the entropy of the system. Hence the rejection of heat by the system leads to a decrease in its entropy.*

  (*b*) *During adiabatic changes, ($\delta q = 0$), the entropy-change is zero. The reversible abiabatic changes are called iso-entropic changes.*

(*iv*) *Entropy is an extensive property. If s denotes the entropy of 1 gm. mol, then the entropy of m gm. mols would be*

$$S = ms$$

The entropy is expressed as cal/degree, which is often stated as entropy units, e.u.

It is very important to remember that the change in entropy must always be computed by taking the system from the initial to the final state *by a reversible path.* Since S is a state function, its change ($\triangle S$) for a given transformation will be the same by whatever path the system changes reversible or irreversible. The ratio of heat absorbed to temperature $\delta q/T$, is not the same for the reversible and the irreversible change, *i.e.*, $\int \frac{\delta q_{rev}}{T} \neq \int \frac{\delta q_{irrev}}{T}$. The entropy-change is only equal to $\int \frac{\delta q_{rev}}{T}$.

This introduction to entropy through a consideration of heat-engines is the classical approach. It is important to realise that in the statements made above, only the 'entropy-change' is defined and not the absolute entropy. Nevertheless, the expression

$dS = \delta q_r/T$ would be found extremely useful in dealing with various phenomena and functions as an excellent tool in building up diverse relations for the properties of a system. It resembles the internal energy whose change is defined as the adiabatic work but its absolute value remains undefined. A more fundamental approach to entropy is based on the probability concepts of statistical mechanics of atomic or molecular compositon of the system. This will be dealt with later.

5.3. Entropy-change in reversible cycles

For a Carnot cycle, it has been shown in eqn. (5.2)

$$\oint \frac{\delta q_r}{T} = 0$$

i.e.,
$$\oint dS = 0 \qquad \ldots (5.3)$$

The entropy-change in the reversible Carnot cycle is nil.

We can now proceed to show that the entropy-change in any reversible cyclic process is zero. Consider a system undergoing a reversible change along the path *ab* in the P-V indicator diagram (Fig. 5*b*). Let us confine our attention to an infinitesimal change *LM* in the path *ab*. This small change may be supposed to be composed of an isothermal change *LN* followed by an adiabatic change *NM*. In this way, the entire change *ab* may be regarded as composed of alternate isothermal and adiabatic changes.

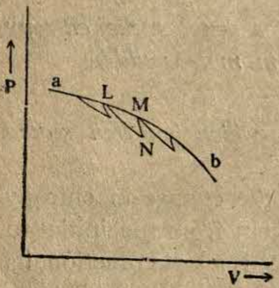


Fig. 5*b*

Now suppose we have a reversible cyclic process, not necessarily a Carnot's cycle, represented by *apbcra* in Fig. 5*c*. We may regard the changes *apb* as well as *cra* consisting of large number of infinitesimal isothermals followed by adiabatics. The adiabatics along *apb* may be joined to those along *cra*. This would turn the complete cyclic process into a large number of Carnot's cycles. Take any one of the Carnot's cycles, say *pqrs*, where *pq* and *rs* are the isothermals with heat-changes, δq_1 at T_1 and δq_2 at T_2 respectively. The heat-changes along the adiabatics *ps* and *qr* are nil.

Then, for the Carnot's cycle *pqrs*, $\dfrac{\delta q_1}{T_1} + \dfrac{\delta q_2}{T_2} = 0$

(δq-terms carry their own signs)

For other Carnot's cycles, similarly,

$$\frac{\delta q'_1}{T'_1} + \frac{\delta q'_2}{T'_2} = 0\,;\ \frac{\delta q''_1}{T''_1} + \frac{\delta q''_2}{T''_2} = 0\,;\ \text{and so on.}$$

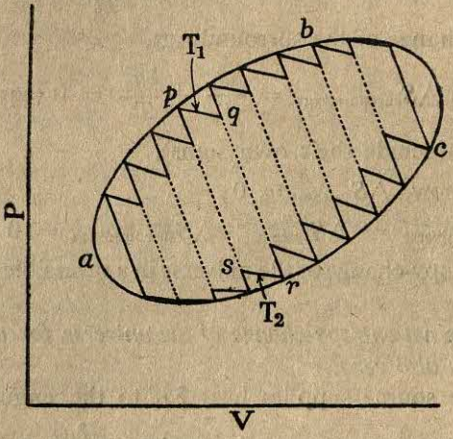


Fig. 5c

Hence for the complete reversible cyclic process,

$$\Sigma\frac{\delta q}{T} = 0\,;\quad \text{or}\ \oint\frac{\delta q}{T} = 0$$

$$\therefore\qquad \oint dS = 0 \qquad \ldots (5.4)$$

i.e., In any reversible cyclic process, the net increase in entropy of the system is zero.

5.4. Entropy-change of the universe

When we speak of the entropy-change of a cyclic process, we consider only the working system but do not take into account the entropy-changes in the source and the sink, *i.e.*, the surroundings. When heat transfer takes place, the surroundings also gain or lose heat and their entropies also change. The total entropy-change which would cover the entropy-changes in the working system as also in the surroundings is named the *entropy-change of the universe*. Hence, the entropy-change of the universe,

$$\triangle S = \triangle S_{\text{system}} + \triangle S_{\text{surroundings}}$$

Let us again consider the Carnot's cycle (Fig. 5*a*) in which the surroundings are the source and the sink.

Now, the loss of entropy of the source $= \dfrac{\delta q_1}{T_1}$

the gain of entropy of the sink $= \dfrac{\delta q_2}{T_2}$

Net entropy change of the surroundings,

$$\Delta S_{\text{surroundings}} = \frac{\delta q_1}{T_1} + \frac{\delta q_2}{T_2} = 0 \text{ (eqn 5.2)}$$

(δq-terms include their own signs).

We already know, $\Delta S_{\text{system}} = 0$

$$\therefore \quad \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

Hence net entropy-change of the universe in a reversible cyclic process is zero.

Again, the *net entropy-change of the universe for a single reversible process is also zero.*

When the source supplies heat δq_1 to the engine, reversibly,

the increase of entropy of the engine $= \dfrac{\delta q_1}{T_1}$

the loss of entropy of the source $= \dfrac{\delta q_1}{T_1}$

That is, the net entropy-change in the reversible transfer of heat from the source to the engine is nil. The same result is obtained when the engine rejects heat to the sink.

5.5. Entropy-change in Irreversible Processes

The entropy-change (dS) is a prefect differential, the entropy-change of a system from a given state I to a given state II is always the same irrespective of the path. Only if the path be reversible, the change would be given by

$$\Delta S = \int_{I}^{II} dS = \int_{I}^{II} \frac{\delta q_r}{T}$$

Hence in order to compute the entropy-change of a system in an irreversible process, we may conceive of taking the system from state I to state II along any reversible path and then divide the heat absorbed at each point by temperature and sum up the quotients.

It may be categorically stated that in any irreversible process, there would be a net increase in entropy. Some simple processes would illustrate it.

(*b*) *Irreversible flow of heat.* Let a heat reservoir at temperature T_1 be brought in contact with a second reservoir at a lower temperature, say at T_2. A small quantity of heat, say q, passes irreversibly from A to B.

The decrease in entropy of $A = q/T_1$

The increase in entropy of $B = q/T_2$

$$\therefore \text{ net entropy-change} = \frac{q}{T_2} - \frac{q}{T_1} = q\,\frac{T_1-T_2}{T_1T_2} = +\text{ ve quantity.}$$

The irreversible flow of heat leads to an increase in entropy.

We can also devise a method for transferring q heat from A to B in a reversible way and then evaluate therefrom the entropy-change. Take an ideal gas in a cylinder and keep it with the hot reservoir at T_1 and reversibly q heat is taken up. [For simplicity we presume that the heat reservoirs have large heat capacities, so that heat-change q scarcely affects their temperatures.] The gas is then removed from A and allowed to expand reversibly and adiabatically until its temperature is T_2. It is then brought in contact with reservoir B and compressed isothermally till q heat is given to B.

The net entropy-change of the two reservoirs $= \dfrac{q}{T_2} - \dfrac{q}{T_1}$ which is the same as before and *positive*.

The net entropy change of the gas-system $= \dfrac{q}{T_1} - \dfrac{q}{T_2}$, hence $-$ *ve*.

The total entropy-change of the gas and reservoirs together is nil, for the whole is a completely reversible cyclic process.

(*ii*) *Irreversible isothermal expansion of an ideal gas.* Suppose n moles of an ideal gas is enclosed in a vessel A of volume v_1. The vessel is connected through a stop-cock to a completely evacauated vessel B of volume v_2. The temperature is T and the system is insulated (Fig. 5*d*).

If the stop-cock is opened, the gas would spontaneously irreversibly expand to the volume $v_1 + v_2$. The work w is zero, and the heat supplied (q) from surroundings is zero. Hence ΔU is zero and temperature remains unaltered.

$$q = \Delta U + w = 0$$

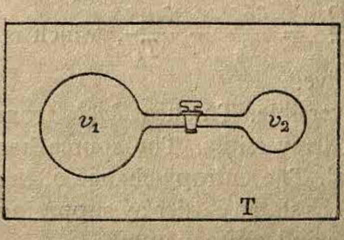


Fig. 5*d*

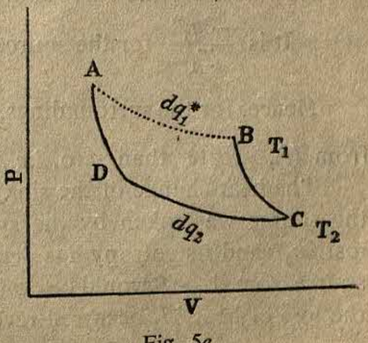


Fig. 5*e*

Now if this expansion of the gas were carried out reversibly at T°K from volume v_1 to volume $(v_1 + v_2)$, the heat absorbed,

$$q_{\text{rev}} = \Delta U + RT\,ln\,\frac{v_1+v_2}{v_1} = 0 + RT\,ln\,\frac{v_1+v_2}{v_1}$$

$$\therefore \qquad \Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} = R\,ln\,\frac{v_1+v_2}{v_1}$$

Since dS is a prefect differential, ΔS_{irr} (system) would be the same.
The surroundings has no thermal-change, hence $\Delta S_{\text{surr}} = 0$
Hence in the irreversible expansion of the gas,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = R\,ln\,\frac{v_1+v_2}{v_1} + 0 = R\,ln\,\frac{v_1+v_2}{v_2} = +\,ve$$

(*iii*) *An irreversible cyclic process*. Consider a cyclic process, similar to that of a Carnot cycle, in which one or more of its stages are performed irreversibly. Let $ABCD$ denote the cycle in Fig. 5*e* in which AB and CD are the isothermal stages. Let us further suppose, the absorption of heat $\delta q_1{}^*$ by the system at temp. T_1 from the source along AB is irreversible. The rest of the stages are carried out reversibly. The asterisk (*) would indicate the irreversibility, otherwise the transformation is reversible. The heat δq_2 is given up to the sink at temp. T_2 along CD.

This is an irreversible cycle and hence the efficiency of the engine is less than that of the Carnot cycle, or,

$$\frac{\delta q_1{}^* - \delta q_2}{\delta q_1{}^*} < \frac{T_1 - T_2}{T_1} \quad \text{or} \quad \frac{\delta q_2}{T_2} - \frac{\delta q_1{}^*}{T_1} > 0 \qquad \ldots (i)$$

When the cycle is completed, the engine has returned to its initial state,

$$\therefore \qquad \Delta S_{\text{system}} = 0$$

Now consder the surroundings and find out the q/T terms.

It is $\dfrac{-\delta q_1{}^*}{T_1}$ for the source and $\dfrac{\delta q_2}{T^2}$ for the sink.

Hence, for the surroundings, $\sum \dfrac{Q}{T} = \dfrac{\delta q_2}{T_2} - \dfrac{\delta q_1{}^*}{T_1}$, which is, from (*i*), greater than zero, *i.e.*, positive.

The heat-change of the sink is reversible. The heat $\delta q_1{}^*$ from the source was taken by the system irreversibly. The source has lost $\delta q_1{}^*$ and its entropy has decreased. The entropy-change of the source from $A \rightarrow B$ would be evaluated as stated earlier by supposing the loss of heat δq_1 occurred reversibly and consequently

$$\Delta S_{\text{source}} = -\delta q_1{}^*/T_1.$$

Or, we can say, $\triangle S_{\text{surr.}} = \frac{\delta q_2}{T_2} - \frac{\delta q_1^*}{T_1} > 0$

In this irreversible cyclic process, therefore

$$\triangle S_{\text{univ.}} = \triangle S_{\text{system}} + \triangle S_{\text{surr.}} = 0 + \triangle S_{\text{surr.}} > 0$$

In an irreversible cyclic process, there would occur a net increase in entropy.

It should be clearly understood that spontaneous changes shall take place in a direction where there would be *net* increase in entropy. It may so happen that the system would undergo a real decrease in entropy and yet the change would be spontaneous for the change in entropy of the system and the surroundings would be positive. If the net entropy-change is negative, the transformation will not occur.

(*iv*) *An irreversible adiabatic process*. We can say, for an irreversible process,

$$\triangle S_{\text{univ.}} = \triangle S_{\text{system}} + \triangle S_{\text{surr.}} > 0$$

It is easy to see that during an irreversible process the entropy of an isolated system will also always increase.

For an irreversible process, we have seen,

$$\triangle S_{\text{system}} + \triangle S_{\text{surr.}} > 0.$$

Since the system is isolated *i.e.*, thermally insulated from the surroundings, the latter will have no change in entropy *i.e.*, $\triangle S_{\text{surr.}} = 0$. Hence,

$$\triangle S_{\text{system}} > 0.$$

That is, *in an irreversible adiabatic transformation, the system will increase in its entropy.*

In other words, *the entropy of an isolated system can never decrease.*

(*v*) *Fall of a weight*. Not only in the transfer of heat-energy, but other irreversible processes lead to the same conclusion. When a weight falls freely, the original potential energy is transferred as heat (q) to the surroundings as it strikes the ground. The net change in entropy is positive and is equal to the heat transferred divided by the temperature. But this operation may be made reversible by attaching, through a pulley, another slightly smaller weight. The first weight would slowly come down and most of its potential energy would be gradually transferred to the second. The process is reversible. The total change in entropy would be practically nil.

(*vi*) *Irreversible flow of heat through a resistor.* Let us consider the chemical process : $Zn + Cu^{++} \rightarrow Cu + Zn^{++}$ as it occurs in a Daniell cell.

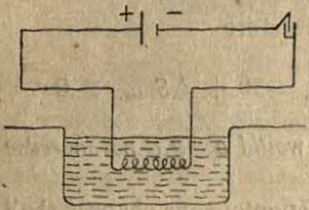


Fig 5*f*

The whole process may be considered as a transfer of two electrons from the zinc atom to the copper ion. Suppose the electrodes are connected through a resistance immersed in a large reservoir (Fig. 5*f*). When the current is switched on, the electricity produced at the expense of the chemical process would be converted into heat and raise the temperature of the reservoir from T to T'. The cell does not gain or lose heat energy but the reservoir receives heat, $\triangle q$. Hence, net gain in entropy :

$$\triangle S = \int_{T}^{T'} \frac{\delta q}{T} = \int_{T}^{T'} C_P \frac{dT}{T} = C_P \ln \frac{T'}{T}$$

Since $T' > T$, there is a net increase in entropy.

These results clearly indicate that all processes proceed in such a direction that the net entropy-change is positive, and approaches zero when the process is reversible. In no process, the net entropy would decrease. This may mathematically be expressed as

$$\triangle S \geqslant 0 \qquad \ldots (5.5)$$

This aspect of the Second law that in all spontaneous changes entropy of the Universe increases helps us in predicting whether a particular reaction will take place or not.

Suppose we have a saturated solution of a salt which is completely isolated from the surroundings, could it crystallise? Now, crystallisation involves decrease in entropy. The system being isolated, $\triangle S_{\text{surr}} = 0$. But $\triangle S_{(\text{net})}$ cannot be negative hence in such a condition crystallisation will not take place.

Again suppose a hot body (T) comes in contact with a cold body (T'). Could some heat flow from the colder to the hotter body? If it flows, loss of entropy for colder body $= q/T'$ and the gain of entropy of hotter body $= q/T$.

The entropy balance $= \frac{q}{T} - \frac{q}{T'} = q\frac{T'-T}{TT'}$ which is negative and hence not possible. Heat would not flow from the colder to the hotter body.

There are cases where apparently a system under consideration seems to lose in entropy. For example, when NO spontaneously reacts with oxygen, entropy decreases. But if we consider the gain in entropy of the surroundings also, there shall be a net gain in entropy.

Entropy and the Second Law : We are thus led to believe that in every irreversible process, if we sum up all the entropy-changes in the different parts of the system and the surroundings, there would be a net rise in the total entropy. In nature, the processes occurring spontaneously are all irreversible. Therefore, *the spontaneous changes in nature would always cause entropy-increase.* Thus, the fall of an apple from a tree, the flowing of a river downhill, the rusting of iron, the dissolution of sugar in water and so on, are all spontaneous and irreversible changes and these would lead to an increase in entropy. In other words, we may say, a natural process will take place in a direction in which the entropy would increase ; or, a process which would not raise the entropy of the universe, will not spontaneously occur. However, in all such changes the energy may be transformed but the total quantity remains constant. This is why the two laws of thermodynamics are often stated as,

(*a*) First Law : *The net energy of the Universe remains constant.*

(*b*) Second Law : *The net entropy of the Universe tends to a maximum.*

5.6. Principle of Caratheodory

In expounding the Second Law we have followed the traditional method of starting with the empirical knowledge that heat flows from higher to lower temperature and that perpetual motion of the second kind is impossible. Use of Carnot's ideal engine led to a mathematical formulation of the law which was subsequently developed by Kelvin and by Clausius to define a new function, entropy S, such that, $\delta q = TdS$. This treatment is most welcome to physicists and engineers, but those who prefer axiomatic development to empirical knowledge, the treatment is unsatisfactory. It was Caratheodory (1909) who enunciated a theorem from which a mathematical deduction of the Second Law was rendered possible, without the aid of any agency like engines. We shall mention here, without going into any detailed description, a very brief outline of Caratheodory's principle.

If a finite space is contemplated with rectangular co-ordinates (x, y, z), then the theorem of Caratheodory states:

"*In the neighbourhood of any given point, P_0, there are other points P which are not accessible from P_0 along solution curves of the equation,*

$A(x, y, z)\,dx + B(x, y, z)dy + C(x, y, z)dz = 0$, *if, and only if, the equation is integrable.*"

Such an equation becomes integrable if it be equivalent to a single finite relation, $F(x, y, z) =$ constant. It can be shown that this will hold if there are functions, $F(x, y, z)$, $\lambda(x, y, z)$ such that

$$Adx + Bdy + Cdz = \lambda dF$$

The mathematical treatment is rather involved and beyond the scope of this text. But the theorem can be extended to a physical system in the following way.

Suppose x, y, z are the thermodynamic co-ordinates which determine the state of the system. Then, the First Law may be expressed as,

$$\delta q = Adx + Bdy + Cdz$$

A, B, C being functions of x, y, z. Under adiabatic conditions, $\delta q = 0$.

$$\therefore Adx + Bdy + Cdz = 0$$

Applying the theorem, we can say,

"*In the neighourhood of any given State P_0 of a physical system, there exist other neighbouring states which are not acceesible from P_0 along adiabatic paths.*" *This is permissible, if and only if, two other functions L and M exist such that* $Adx + Bdy + Cdz = LdM$, or $\delta q = LdM$. In reality these two functions are T ana S, so that

$$\delta q = TdS$$

which is our familiar form of the Second Law. It is hence possible to enunciate the Law using Caratheodory's principle which introduces the function S.

We can examine it a little further. Suppose δq_1, δq_2, etc, be the quantities of heat taken up by different parts of a system (heterogeneous systems not excluded), then the total heat δq entering the system is given by:

$$\delta q = \delta q_1 + \delta q_2 + \delta q_3 + \dots$$

From the first law, each δq-term may be expressed as

$$\delta q_1 = \left(\frac{\partial U}{\partial z_1}\right) dz_1 + p_1 dv_1$$

where $z_1, \dots$ etc. are variables for U_1.

Hence, δq may be written as,

$$\delta q = Z_1 dz_1 + Z_2 dz_2 + \dots$$

where Z_1, Z_2 are functions of variables determining the state of the whole system. It may be remembered, in an adiabatic change $\Sigma Z_1 dz_1 = 0$.

Take a system containing a single substance and for the sake of simplicity let it be a system of a mole of perfect gas. Then

$$\delta q = C_v dT + pdv = C_v dT + \frac{RTdv}{v}$$

The rt. hand side is not generally integrable, but if we divide by T, then

$\frac{\delta q}{T} = C_v \frac{dT}{T} + \frac{Rdv}{v}$. becomes integrable and we nave a definite value for $\delta q/T$. Let this be expressed by the symbol S and be called entropy. Obviously,

$$\frac{\delta q}{T} = f(v,T), \text{ and } S = \int \frac{\delta q}{T}$$

or

$$\delta q = TdS$$

We have come to this result without assuming the Second Law or the use of heat-engines. The multiplying factor $1/T$ which makes the expression integrable is called the 'integrating factor'. Since $\delta q = Tds$, and in an adiabatic process $\delta q = 0$, hence $dS = 0$, or S is constant.

In other words, in an adiabatic process, all the states that may arise must be represented by co-ordinates of the curve having a constant S. Any state represented by a point outside this curve, even very close to it, cannot be reached by an adiabatic change. This substantiates the principle of Caratheodory. But more interesting is the fact that this can be extended to systems defined by more than two variables.

Suppose two systems K, K', whose variables are v_1, T_1 and v_2, T_2 are brought together. If these be in thermal equilibrium, $T_1 = T_2 = T$ (say). There are, therefore, three variables for the whole system. Then,

$$\delta q = \delta q_1 + \delta q_2$$

And for individual systems we know, $\delta q_1 = T_1 dS_1$ and $dq_2 = T_2 dS_2$.

For the whole system,

$$\delta q = \left(\frac{\partial U_1}{\partial v_1} + p_1\right) dv_1 + \left(\frac{\partial U_2}{\partial v_2} + p_2\right) dv_2 + \left(\frac{\partial U}{\partial T}\right) dT$$

In adiabatic transition, the rt.-hand expression should be zero. The adiabatic process is subject to the condition,

$$A dv_1 + B dv_2 + C dT = 0$$

where A, B, C are functions of the variables, v_1, v_2 and T.

Now, the condition $\delta q = 0$ is possible only if there be definite points which can be reached by adiabatic process and no other point in the neighbourhood is accessible by the adiabatic change. In these circumstances, $A dv_1 + B dv_2 + C dT = 0$, implying $dS = 0$, or S is constant.

We can then say, $\delta q = TdS$ or $TdS = T_1 dS_1 + T_2 dS_2$

for the given system.

Since $T_1 = T_2 = T$, we have $dS = d(S_1 + S_2)$. We can thus conclude that for any such system there exists a function S.**

5.7. Entropy and the available work

A little reflection would reveal that with the progress of an irreversible process, the possibility of obtaining work from a system diminishes.

Suppose there are three heat reservoirs at high temperatures T_1, T_2, and T_3 such that $T_1 > T_2 > T_3$. There is also another heat

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**Caratheodory, Math. Annalen, 67, 355 (1909), Buchadahl, Am. J. of Physics, Jan, 1949.

reservoir, the sink, at a lower temperature T (Fig 5g). Let there be a reversible engine working between the 1st reservoir at T_1 and the sink at T and let the quantity of heat supplied to the engine from the source at T_1 be Q. Then we know that the maximum work available would be,

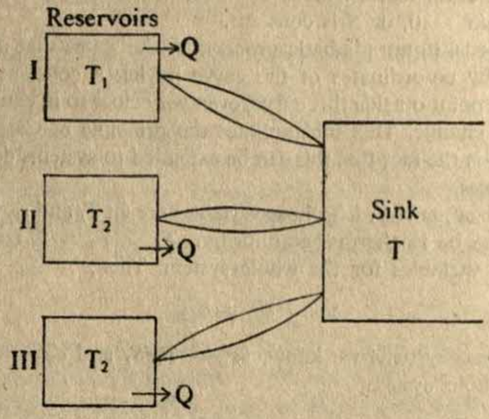

Fig. 5g

$$W_1 = Q\left[1 - \frac{T}{T_1}\right]$$

Let us imagine next that the heat Q have flown down irreversibly from the 1st reservoir at T_1 to the second reservoir at T_2 by conduction or radiation before being received by the engine. Now, suppose we engage a reversible engine to work between the second reservoir and the sink and let the engine receive the same heat Q from this source. The maximum work available would be,

$$W_2 = Q\left[1 - \frac{T}{T_2}\right]$$

Similarly, if the heat Q flows down irreversibly to the third reservoir at T_3 and then supplied to a reversible engine as before, the maximum available work would be

$$W_3 = Q\left[1 - \frac{T}{T_3}\right]$$

The amount of work available from the same quantity of heat supplied are different. Since $T_1 > T_2 > T_3$ it is easily seen that $W_1 > W_2 > W_3$.

This means that the lower the temperature of the reservoir to which the amount of heat Q would irreversibly flow, the lesser would be the yield of work. If in this way the same heat Q flows down to a reservoir at T (the same as that of the sink), the available work $\left[W = Q\left(1 - \frac{T}{T}\right)\right]$, would be nil. Though the quantity of heat remains the same, yet due to its irreversible transfer from the higher to the lower temperature, its potentiality of being converted into work is diminished or degraded. This is why the first law is often called as the law of conservation of energy and the second law as the law of degradation of energy.

Let us come back to the question of the availability of work. Due to irreversible flow of heat from T_1 to T_2 the decrease in the amount of available work,

$$\triangle W' = W_1 - W_2 = Q\left[\frac{T}{T_2} - \frac{T}{T_1}\right] = QT\frac{T_1 - T_2}{T_1 T_2}, \text{(a + \textit{ve} quntity)}$$

Again, due to the irreversible flow of heat, the increase of entropy,

$$\triangle S = \frac{Q}{T_2} - \frac{Q}{T_1} = Q \cdot \frac{T_1 - T_2}{T_1 T_2}$$

By substitution, $\triangle W' = T\triangle S$ . . . (5.6)

That is, the energy rendered unavailable as work is proportional to the entropy-increase. The higher the level of entropy, the lesser would be the availability of work. The entropy-rise is a measure of the unavailable work.

A system left to itself will *irreversibly* approach the state of eqm, with consequent increase in entropy. It has just been shown that with increase in entropy, the unavailability of work from the system also increases. When the system attains eqm, the entropy reaches its maximum value and the availability of work becomes nil. The entropy thus reveals the state of the system as to its capability of yielding work. Since entropy (S) reaches its maximum at eqm, for any virtual change of the system at eqm, $dS = 0$.

5.8. Concept of Entropy

From our previous discussion, we have seen that entropy is a state function and it has two characteristics. Firstly, in any spontaneous, and hence irreversible, change the net-entropy always increases. Secondly, every system always tries to attain equilibrium and as the system approaches equilibrium, its entropy increases. When eqm in reached, entropy becomes maximum and constant. At the same time, with approach towards equilibrium, the capacity of the system to yield work goes on diminishing and at equilibrium, no work is available from the system, as if the system is completely exhausted or run-down. Entropy is thus an index of the condition or character of the system.

To wit : The amount of available work from a given heat-source diminishes with fall in temperature of the source. When the source and the sink are in thermal equilibrium *i.e.*, same temperature, the entropy is maximum but the available work is nil (Sec. 5.7). That is, the more the system is run down, the greater is the entropy. Again if we take a voltaic cell and complete the circuit externally, we obtain electrical work so long as there is a potential difference between the two electrodes. With the performance of work, the potential difference between the two electrodes diminishes. When the two electrodes attain the same potential, the entropy increases but the cell is completely run down and would yield no work. This is why the entropy is considered as the run-down-ness of a system.

A better understanding of entropy emerges when the system is looked at from the kinetic molecular hypothesis. A system, when it attains equilibrium, has maximum disorder or chaos of its constituent atoms or molecules under the given set of parameters. That is, the state of equilibrium means a state of maximum chaos. For example, (*i*) if a gas confined in a flask is allowed to expand freely into another flask attached to it, the motion of the molecules of gas becomes more random or chaotic and we have seen the entropy of the system increases [Sec 5.5 (*ii*)]. The entropy increases with increase in the disorder. (*ii*) Again, if we let loose a small amount of yellowish green chlorine gas in this room, it will immediately spontaneously diffuse through the entire air until equilibrium is attained *i.e.*, its concentration becomes the same at every point. This spontaneous mixing leads to an increase in entropy (Sec. 5-14). Exactly similar are the processes when a syrup gets diluted by diffusion in the water added to it or a piece of zinc added to dil. H_2SO_4 dissolves. (*iii*) If one end of a poker is placed in an oven, the red hot end distributes its heat and raises the temperature of the entire rod. The rise of temperature means more vigorous motion of the atoms and meantime the entropy rises by acquisition of heat. (*iv*) Arrange a number of red and black balls in a tray side by side and then shake the tray vigorously for some time, the two types of balls would mix up in the most disordered fashion. This is irreversible and the opposite would not happen in nature. The entropy increases.

The more a system approaches equilibrium the greater is the disorder and irreversibility. When equilibrium is reached it has maximum disorder. The entropy also goes on increasing and reaches its maximum value at the equilibrium state. In other words, the entropy is a measure of the disorder of the system or it may be called a measure of the mixed-up-ness of the system.

Conversely, when we attempt to bring order to a system entropy diminishes. Suppose we have a gas in equilibrium confined in a cylinder with a piston. The piston is now somewhat raised upwards increasing the volume slightly. All the molecules, in whatever direction those might be moving, are subjected now to a tendency of motion in the direction of the piston. This is indirectly an attempt to bring some order. In consequence, the gas is cooled and the entropy decreases. We shall see later, in the crystalline state of pure substances the entropy becomes the least as there is perfect order or least chaos.

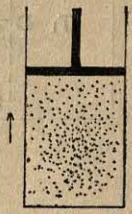

Fig. 5*h*

In a solid, the atoms remain in a perfectly ordered arrangement. When the solid melts, the atoms (or molecules) move to some extent freely and randomly, *i.e.*, disorder increases. And during melting, the entropy increases from absorption of heat. Similarly when a liquid vaporises, the molecular motion in the gas phase becomes most chaotic. Meanwhile, the entropy increases, *i.e.*, $\triangle S$ is positive. Thus,

(*a*) in the melting of benzene, $\triangle S = \dfrac{L_f}{T} = \dfrac{78 \times 30.3}{278.3} = 8.4$ e.u.

(*b*) in the vaporisation of benzene, $\triangle S = \dfrac{L_v}{T} = \dfrac{78 \times 131.5}{353.2} = 29.04$ e.u.

The increase in entropy is thus a measure of the disorder in a system. A precise and mathematical relation between this disorder and the entropy will be discussed in a later section.

5.9. T-S diagrams

Usually in the graphical presentation of the state of a material system, the variables *P* and *V* are employed. But it is also possible to use the variables *S* and *T* instead, plotting temperatures along the Y-axis and entropies along the X-axis. In such representation, an adiabatic-change will be a vertical straight line parallel to the *T*-axis and an isothermal change will be a horizontal line parallel to the *S*-axis.

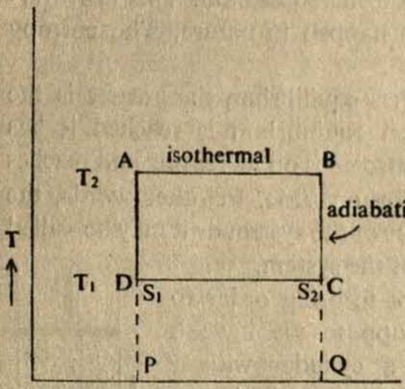

Fig. 5*i*

The Carnot's cycle then will take the rectangular form as shown in Fig. 5*i*. *AB* and *CD* are the isothermals while *BC* and *DA* are the adiabatics.

In the isothermal change *AB*, the heat (Q_1) received from the source,

$$Q_1 = T\triangle S = T_2(S_2 - S_1) = \text{AP} \times \text{BA} = \text{area ABPQ}$$

and during the isothermal compression, the heat (Q_2) given out to the sink,

$$Q_2 = T\triangle S = T_1(S_2 - S_1) = \text{DP} \times \text{DC} = \text{area CDPQ}.$$

Hence, work $W = Q_1 - Q_2 =$ area ABPQ − area CDPQ = area ABCD.

The area, ABCD enclosed within the *T-S* diagram denotes the work, This is also employed in other types of cycles. e.g. Otto-cycle or diesel cycles (See diagrams 4*j* and 4*m*).

Problem : Compare the efficiencies of the cycles *abca* in the figures I and II below :

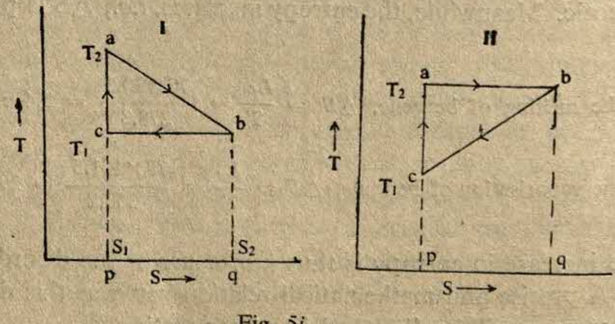

Fig. 5*j*

In I, the heat supplied, [area *abqp*] $= T_1(S_2-S_1) + \frac{1}{2}(T_2-T_1)(S_2-S_1)$ and the work obtained $= \frac{1}{2}(T_2-T_1)(S_2-S_1)$

$$\therefore \epsilon_1 = \frac{\frac{1}{2}(T_2-T_1)(S_2-S_1)}{\frac{1}{2}(T_2-T_1)(S_2-S_1) + T_1(S_2-S_1)} = \frac{T_2-T_1}{T_2+T_1}$$

In II, the heat supplied [area *abpq*] $= T_2(S_2-S_1)$
and the work obtained $= \frac{1}{2}(T_2-T_1)(S_2-S_1)$

$$\therefore \epsilon_2 = \frac{\frac{1}{2}(T_2-T_1)(S_2-S_1)}{T_2(S_2-S_1)} = \frac{T_2-T_1}{2T_2}$$

$$\therefore \frac{\epsilon_1}{\epsilon_2} = \frac{2T_2}{T_1+T_2}$$

5.10. Entropy relation with Internal Energy and Enthalpy

By definition, $\frac{\delta q_r}{T} = dS$

or $\delta q_r = TdS$ . . . (5.7)

From the First Law, $\delta q_r = dU + PdV$

or $dU = \delta q_r - PdV$

i.e. $dU = TdS - PdV$ . . . (5.8)

Hence, $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $-\left(\frac{\partial U}{\partial V}\right)_S = P$ . . . (5.9)

These are important thermodynamic definitions for temperature and pressure.

Again, for an enthalpy change,

$$dH = dU + PdV + VdP = \delta q_r + VdP$$

i.e. $dH = TdS + Vdp$ . . . (5.10)

Hence, $\left(\frac{\partial H}{\partial S}\right)_P = T$ and $\left(\frac{\partial H}{\partial P}\right)_S = V$ . . . (5.11)

5.11. Temperature dependence of Entropy

From (5.8), $TdS = dU + pdV = C_V dT + pdV$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}\text{; or } \triangle S = \int_{T_1}^{T_2} \frac{C_V}{T}\,dT = C_V \ln\frac{T_2}{T_1} \quad \ldots (5.12)$$

Likewise, from (5.10) ,

$$TdS = dH - VdP = C_P dT - VdP$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}\text{, or } \triangle S = \int_{T_1}^{T_2} \frac{C_P}{T}\,dT = C_P \ln\frac{T_2}{T_1} \quad \ldots (5.12)$$

[C_P, C_V are supposed to remain unaltered]

As C_P/T and C_V/T are positive, the entropy always increases with temperature.

5.12. Entropy of an ideal gas

It is possible to express the entropy of a prefect gas now from the first law,

$$\delta q = dU + PdV$$

Dividing both sides by T,

$$\frac{\delta q}{T} = \frac{dU}{T} + \frac{PdV}{T} = C_V\frac{dT}{T} + R\frac{dV}{V} \quad \text{(for 1 gm. mol)}$$

$$\text{or} \quad dS = C_V d\ln T + R d\ln V$$

$$\text{or} \quad S = C_V \ln T + R\ln V + S_o \qquad \ldots (5.14)$$

[Where S_0 is a constant ; heat-capacities assumed to remain unaltered.]

Since $C_P - C_V = R$ for a perfect gas, hence

$$S = (C_P - R)\ln T + R\ln\frac{RT}{P} + S_o$$

$$\text{or} \quad S = C_P\ln T - R\ln P + S_o' \qquad \ldots (5.15)$$

$$\text{Again,} \quad S = C_P\ln\frac{PV}{R} - (C_P - C_V)\ln P + S_o'$$

$$= C_P\ln V + C_V\ln P + S_o'' \qquad \ldots (5.16)$$

It must be noted here that the value of the constant S_o cannot be obtained from the thermal capacities or the parameters alone. As such, we cannot ascertain the absolute value of the entropy of a perfect gas from these relations. But the changes in entropy can be easily determined. Thus if the temperature of a gas changes from T_1 to T_2 and volumes from V_1 to V_2 then, for one gm. mol of the gas,

$$S_1 = C_V\ln T_1 + R\ln V_1 + S_o,$$

$$S_2 = C_V\ln T_2 + R\ln V_2 + S_o$$

$$\therefore \; \Delta S = C_V\ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1} \qquad \ldots (5.17)$$

For isothermal changes, $\Delta S = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2}$ . . . (5.18)

Real Gases : The entropy may be expressed as follows:

$$S = f(T,V)$$

$$\therefore \qquad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \frac{C_V}{T}\, dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Anticipating an important Maxwell relation (see next chapter), $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, we can write,

$$dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$$

If the gas be a van der Waals one, then

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}.$$

Hence, $$dS = C_V \frac{dT}{T} + \frac{R}{V-b} dv$$

$$= C_V d \ln T + R d \ln (V-b)$$

$$\therefore\ S = C_V \ln T + R \ln (V-b) + \text{constant}$$

$$\triangle S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2-b}{V_1-b} \qquad \ldots (5.19)$$

5.13. Entropy of an ideal gas at standard state

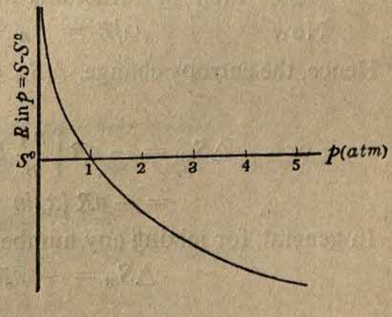

Fig. 5k

In order to give quantitative values for entropy, a standard state of the system has to be prescribed. Usually, a temperature of 25°C and 1 atm. pressure are accepted for the standard state of the system.

If S and S° denote the entropies at pressure p atm and at 1 atm for a mole of an ideal gas, temperature being consant at 25°C, then from eqn. (5.18),

$$S - S^\circ = -R \ln \frac{p \text{ atm}}{1 \text{ atm}} = -R \ln p \qquad \ldots (5.20)$$

A plot of p against $S-S^\circ$ (Fig. 5k) would reveal the nature of variation of entropy with pressure-change. We shall see later how S° can be evaluated with the help of the third law. This will help in estimating the entropy at any other pressure.

5.14. Entropy-Change in mixture of gases

Two or more gases when brought in contact would immediately diffuse into one another and mix up irreversibly. This spontaneous irreversible process of mixing leads to an increase in entropy. The entropy-increase is expressed as follows:

Let n_A and n_B gm-moles of two *ideal* gases A and B be mixed a constant pressure P and a constant temperature T. Before mixing their entropies are:

$$S_A = n_A \left[C_{P_A} \ln T - R \ln P + S_A{}^0 \right]$$

$$S_B = n_B \left[C_{P_B} \ln T - R \ln P + S_B{}^0 \right]$$

After mixing, the total pressure P remains constant. The partial pressures are p_A and p_B, such that $P = p_A + p_B$.

The entropies of the two components in the mixture are:

$$S_{A_m} = n_A \left[C_{P_A} ln\, T - R\, ln\, p_A + S_A{}^0 \right]$$

$$S_{B_m} = n_B \left[C_{P_B} ln\, T - R\, ln\, p_B + S_B{}^0 \right]$$

The entropy-change due to mixing ; $\triangle S_m = S_{A_m} + S_{B_m} - S_A - S_B$

or $$\triangle S_m = -n_A R\, ln\, (p_A/P) - n_B R\, ln (p_B/P)$$

The total amount of the mixture, $n = n_A + n_B$ moles

Hence their mol-fractions are $x_A = n_A/n$, and $x_B = n_B/n$

Now $$p_A/P = x_A \quad \text{and} \quad p_B/P = x_B$$

Hence, the entropy change, $\triangle S_m = -n_A R\, ln\, x_A - n_B R\, ln\, x_B$ . . . (5.21)

or $$\triangle S_m = -nR \left[\frac{n_A}{n}\, ln\, x_A + \frac{r_B}{n}\, ln\, x_B \right]$$

$$= -nR \left[x_A ln\, x_A + x_B ln\, x_B \right] \qquad \text{. . . (5.22)}$$

In general, for mixing any number of gases,

$$\triangle S_m = -nR\, \Sigma x_i\, ln\, x_i \qquad \text{. . . (5.23)}$$

Problem : At N.T.P., 2.8 litres of oxygen were mixed with 19.6 litres of hydrogen. Calculate the increase in entropy.

$$2.8 \text{ litres of oxygen} = \frac{2.8}{22.4} = 1/8 \text{ gm-mole}$$

19.6 litres of hydrogen $= \frac{19.6}{22.4} = \frac{7}{8}$ gm-mole ; Total = 1 gm-mole

Hence mol-fraction of $O_2 = \frac{1}{8}$, mol-fraction of $H_2 = \frac{7}{8}$

$\therefore$ The entropy-change $= -\frac{1}{8} R \ln \frac{1}{8} - \frac{7}{8} R \ln \frac{7}{8} = 0.754$ calories/degree

5.15. Entropy-Change in a chemical process

As stated before the characteristic value of the entropy of a substance at 25°C and 1 atm is taken as the standard entropy of the same. The standard values of entropy of different substances have been tabulated and are readily available.

It will be shown later that the entropy of a pure crystalline substance at 0°K is zero ; $S^\circ_{0.K} = 0$.

From equation (5.13),

$$\triangle S = \int_0^T C_P \frac{dT}{T} = \int_0^T C_P d \ln T$$

By measuring C_P of the substance from 0°K to 298°K and plotting them against lnT, it is easily possible to compute the value of standard entropy of the substance (see Chap. 8). S° can also be obtained from statistical data.

In a chemical process, the standard entropy-change is the difference of the standard entropies of the products and the reactants. In the reaction ; $mA + nB \rightarrow pC + qD$,

$$\triangle S = pS^\circ_C + qS^\circ_D - mS^\circ_A - nS^\circ_B$$

To illustrate :

(*i*) Take the reaction : $SO_2Cl_2 + H_2O \longrightarrow SO_2 + 2HCl$

	SO_2Cl_2	H_2O	SO_2	$2HCl$	
S°_{298}-values	216	69.9	248	187	J/mole°K

$$\therefore \triangle S = S^\circ_{SO_2} + 2S^\circ_{HCl} - S^\circ_{SO_2Cl_2} - S^\circ_{H_2O}$$

$$= 248 + 2 \times 187 - 216 - 69.9 = +338.1 \text{ J/mole°K}$$

(*ii*) The synthesis of ammonia : $\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3$

	$\frac{1}{2}N_2$	$\frac{3}{2}H_2$	NH_3	
S°-values	45.8	31.2	46.03	Cal/mol°K

$$\therefore \triangle S = S^\circ_{NH_3} - \tfrac{1}{2} S^\circ_{N_2} - \tfrac{3}{2} S^\circ_{H_2}$$

$$= 46.03 - \tfrac{1}{2} \times 45.8 - \tfrac{3}{2} \times 31.2 = -23.67 \text{ Cal/mol°K}$$

5.16. Calculation of entropy-change in some simple processes

Problem : What would be the change in entropy when 1 Kg. water at 7°C is mixed with 2 Kg. water at 37°C in an insulated vessel?

On mixing let the final temperature be t°C.

Then, $1(t-7) = 2\times(37-t)$; or $t = 27°\text{C} = 300°\text{K}$

$$\text{The entropy-change, } \Delta S = 1000 \ln \frac{300}{280} + 2000 \ln \frac{300}{310} = 2.99 \text{ cal/°K}$$

Problem : What would be the change in entropy if five moles of an ideal gas be doubled in volume isothermally?

$$\Delta S = 5 \times R \ln \frac{V_2}{V_1} = 5\times 1.98\times 2.303 \log 2 = 6.9 \text{ e.u.}$$

Problem : What would be the change in entropy when ten gm tin is heated from 293°K to 573°K. The m. pt. of tin is 505°K. Its latent heat of fusion 14 cal/gm, sp. heat of solid tin and liquid tin are 0.055 and 0.064 respectively.

(*i*) Entropy-change in heating 10 gm. of tin from 293°K to 505°K (m.pt),

$$\Delta S_1 = \int_{293}^{505} mc \frac{dT}{T} = 10 \times 0.055\, ln \frac{505}{293} = 0.2994$$

(*ii*) entropy-change in the fusion of tin,

$$\Delta S_2 = \frac{\Delta q}{T} = \frac{10 \times 14}{505} = 0.28$$

(*iii*) entropy-change in heating liquid tin from 505°K to 573°K

$$\Delta S_3 = \int_{505}^{573} \frac{dq}{T} = \int_{505}^{573} 10 \times 0.064 \frac{dT}{T} = 0.081$$

The total entropy-change, therefore,

$$\Delta S_1 + \Delta S_2 + \Delta S_3 = 0.2994 + 0.28 + 0.081 = 0.6604 \text{ e.u.}$$

Problem : Find the increase in the molar entropy of copper when it is heated from 127°C to 927°C. The molar sp. heat of copper is given by $C_P = 6.2 + 0.0017T$

$$\Delta S = \int_{400}^{1200} \frac{C_P dT}{T} = \int_{400}^{1200} \frac{(6.2 + 0.0017T)}{T} dT$$

$$= 6.2\, ln \frac{1200}{400} + 0.0017\,(1200-400) = 9.77 \text{ e.u.}$$

Problem : Given, specific heat of liquid water = 4180 joules per kg., specific heat of water vapour = $(1670 + 0.49T)$ joules per kg. and latent heat of vaporisation = 23 × 10^5 joules per kg., compute the change in entropy when 100 Kg. of water at 27°C are converted into superheated steam at 200°C under constant atmospheric pressure.

(*i*) The entropy-change in heating water from 27°C to 100°C,

$$\triangle S_1 = 100 \int_{300}^{373} C_P d\ln T = 100 \times 4180 \times 2.303 \log \frac{373}{300} = 91082.2$$

joules/degree C

(*ii*) the entropy-change in vaporisation,

$$\triangle S_2 = 100 \times \frac{23 \times 10^5}{373} = 6.2 \times 10^5 \text{ joules/degree C.}$$

(*iii*) the entropy-change in heating steam from 100°C to 200°C,

$$\triangle S_3 = 100 \int_{373}^{473} C_P \frac{dT}{T} = 100 \int_{373}^{473} \frac{(1670 + 0.49T)}{T} dT$$

$$= 100 \times 1670 \ ln \frac{473}{373} + 0.49 \times 100 \times (473 - 373)$$

= 39696 joules/degree °C.

Total entropy-change = 91082.2 + 6.2 × 10^5 + 39696
= 7.5 × 10^5 joules per degree °C.

Problem. A current of 10 amperes is passed for a second through a resistance-wire of 20 ohms. The resistance-wire weighed 5 gm. ; its initial temperature was 10°C ; sp. heat = 0.85 joules per gm. Calculate the entropy-change.

Heat produced = $10^2 \times 20 \times 1$ = 2000 joules

If $\triangle t$ be the rise in temperature of the wire, then

$$2000 = 5 \times 0.85 \times \triangle t, \quad \text{or } \triangle t = 470° \text{ app.}$$

The final temerature of the wire = 480°C = 753°K

$$\text{The entropy-change, } \triangle S = 5 \times 0.85 \ln \frac{753}{283} = 4.16 \text{ joules/degree.}$$

Problem : One mole of an *ideal* gas is isothermally compressed at 400°K from 2 atm to 20 atm. The surroundings are a bath at constant temperature of 300°K. Calculate the total entropy-change when (*i*) the process is reversible and (*ii*) when the process is irreversible requiring 10% more work than in the reversible compression.

(*i*) *Reversible Process*

$$Q = \triangle U + w = 0 + RT \ ln \frac{2}{20} \qquad \text{(ideal gas)}$$

$$= 2.303 \times 8.314 \times 400 \ (-1) \ J$$

$$= -7659 \ J$$

$$\therefore \triangle S_{\text{System}} = Q/T = -7659/400 = -19.148 \ J/°\text{K}$$

[This entropy-change for the system would be the same whether the process is reversible or not.]

Now, $\Delta S_{\text{Surr}} = Q/T_{\text{Surr}} = 7659/300 = +\ 25.530\ J/°K$

$\therefore\ \Delta S_{\text{total}} = \Delta S_{\text{Sys}} + \Delta S_{\text{Surr}} = -\ 19.148 + 25.530 = +\ 6.328\ J/°K$

(ii) Irreversible Process

$$\text{work reqd} = -\ 7649 \times \frac{110}{100} = -8425\ J$$

i.e., $Q = -\ 8425\ J$

We know, $\Delta S_{\text{Sys}} = -\ 19.148\ J/°K$

$\Delta S_{\text{Surr}} = Q/T_{\text{Surr}} = +\ 8425/300 = +\ 28.08\ J/°K$

$\therefore\ \Delta S_{\text{Total}} = \Delta S_{\text{Sys}} + \Delta S_{\text{Surr}} = -\ 19.148 + 28.08 = 8.932\ J/°K$

Problem : Calculate the entropy-change at 1 atm for the fusion of a mole of ice into water at −20°C. Given, latent heat of fusion of ice at 0°C = 6040 *J*/mole. $C_{P_l} = 75.6$ and $C_{P_s} = 37.2$ *J*/mole-K.

The entropy-change has to be computed in three steps

(*i*) Heat 1 mole ice from −20°C to 0°C (m. pt)

$$\Delta S_1 = \int_{253}^{273} \frac{dq}{T} = \int_{253}^{273} C_p d\ln T = 2.303 \times 37.2 \log \frac{273}{253}$$

$$= 5.762\ J/\text{mole-}°K$$

(*ii*) Melt 1 mole of ice at 0°C,

$$\Delta S_2 = \frac{L_f}{T} = \frac{6040}{273} = 22.12\ J/\text{mole-}°K$$

(*iii*) Cool 1 mole of water from 0°C to −20°C,

$$\Delta S_3 = \int_{273}^{253} \frac{dq}{T} = \int_{273}^{253} C_p d\ln T = 2.303 \times 75.6 \log \frac{253}{273}$$

$$= -2.835\ J/°K\text{-mole}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 5.762 + 22.12 - 2.835 = 25.047\ J/\text{mole-}°K$$

Problem : One mole of an ideal diatomic gas ($C_v = 5.00$) initially at 25°C and 1 atm changes to 100°C and 10 atm pressure. Calculate the entropy change. What will be its entropy in the final state if the standard molar entropy of the gas at 25°C and 1 atm be 45.80 *e.u.*

(*i*) The entropy-change due to changes in temp. and pressure,

$$\Delta S = C_p ln \frac{T_2}{T_1} - R ln \frac{p_2}{p_1}$$

$$= 7 \times 2.303 \log \frac{373}{298} - 2 \times 2.303 \log \frac{10}{1} = -\ 3.02\ e.u.$$

(*ii*) At 25°C and 1 atm, absolute entropy, $S° = 45.80$ *e.u.*/mole

$\therefore$ At 100°C and 10 atm, the entropy

$S = S° + \Delta S = 45.80 - 3.02 = 42.78\ e.u.$

Problem : 20 litres nitrogen at 100 atm and 200°C expands adiabatically against a constant external pressure of 1 atm till eqm is attained. [C_p = 7.0 cal/mole-°K]. Calculate $\triangle S$ for the change.

Let there be n mole of gas and suppose the final volume and temperature be V_2 and T_2.

$$n = P_1V_1/RT_1 = 100 \times 20/(0.082 \times 473) = 51.56$$

Since the process is adiabatic, $q = 0$, hence

$$\triangle U = -W$$

$$nC_V(T_2-T_1) = -P_2(V_2-V_1)$$

$$\text{or} \quad nC_V[(P_2V_2/nR)-T_1] = -P_2(V_2-V_1)$$

$$\text{or } V_2 = \frac{nC_VT_1 + P_2V_1}{P_2 + C_VP_2/R} = \frac{51.56 \times (5 \times 0.0413) \times 473 + 1 \times 20}{1 + 5/2}$$

$$= 1437.5 \text{ litres}$$

$$\therefore T_2 = \frac{P_2V_2}{nR} = \frac{1 \times 1437.5}{51.56 \times 0.082} = 339.8°\text{K}$$

Hence the entropy-change,

$$\triangle S = n\left[C_P ln \frac{T_2}{T_1} - R\, ln \frac{P_1}{P_2} \right]$$

$$= 2.303 \times 51.56 \left[7.\ \log \frac{339.8}{473} - 2 \log \frac{1}{100} \right]$$

$$= 352.15 \ e.u.$$

Though adiabatic $\triangle S \neq 0$, for the process is irreversible.

5.17. Entropy and Probability

Suppose a small container filled with a gas, say chlorine, is placed at the corner of a room and its lid is removed. The gas molecules would immediately spontaneously move in diverse direction. The spread of the molecules will not cease after occupying only a quarter or half of the room. The molecules would move on until the whole room is filled up. The most randomised dispersal proceeds until the equilibrium it set up. The system thus changes spontaneously in a direction that corresponds to a greater dispersal of energy. Never do we find that the molecules would return to the orginal container or to a smaller volume leaving the rest of the room vacant. The probability of the gas being fully dispersed occupying the whole space is much greater than the probability of its occupying only a fraction of the space. The direction of a spontaneous change is from a state with low probability occurring to one of maximum probability. We have further seen that at eqm. when maximum dispersal occurs the entropy is also maximum. A relation between the entropy and the randomness of distribution of the molecules is thus anticipated.

A. The possible distributions : Macrostates/Microstates

To understand the distribution of particles in a system, we may start with some examples.

(*i*) Let there be four points *p*, *q*, *r* and *s* to be placed in two cells *x* and *y*. The distribution of the four points in *x* and *y* may be made in the following five ways :

Cell *x*	4	3	2	1	0
Cell *y*	0	1	2	3	4

That is, there are five broad patterns of distribution of the four points in the two cells, irrespective of which points occupy *x* or *y*. These are named 'macrostates' of the system. If we now select any one of these macrostates, say the distribution 2 : 2, then the possible ways of the placement of the points in *x* and *y* cells would be:

Cell *x*	*pq*	*pr*	*ps*	*qr*	*qs*	*rs*
Cell *y*	*rs*	*qs*	*qr*	*ps*	*pr*	*pq*

(The internal arrangement within any cell is ignored.)

It is thus seen that there are as many as six possible ways in which the distribution (2:2) can be realised. This detailed picture of the distribution of particles for a given macrostate is known as a 'microstate'. For every macrostate there may be one or more microstates.

(*ii*) Let us take another example. There are two dice *P* and *Q*. On rolling the dice, any of the six sides may turn up ; one face is just as likely to turn up as another. Let the number turning up on *P* be denoted by *P*1, *P*2, . . . *P*6 and those on *Q* be denoted by *Q*1, *Q*2, . . . *Q*6. Now, if the two dice be rolled together, the *sum of the numbers* (*S*) turning up on the two dice may be from 2 to 12. In all there are 36 possible combinations. If we want a particular sum to turn up, (i.e. a particular pattern or macrostate) there may be one or more ways. For example, to obtain *S*12, there is only one way *P*6*Q*6. But if want the sum to be eight (*S*8), then the chances are *P*2*Q*6, *P*6*Q*2, *P*3*Q*5, *P*5*Q*3, *P*4*Q*4; that is, there are five 'microstates' by which the macrostate (*S*8) can exist. One microstate is as possible as any other. For the macrostate (*S*12) there is only one configuration or microstate, whereas for *S*8, there are five. It is thus seen that the macrostate which would be most observed is the most probable state.

(*iii*) Let us next consider a system containing a number of monatomic particles. The total energy *U* of the system is shared by the individual particles. But according to quantum principles, a particle cannot have any amount of energy. Only some discrete values of energy are allowed to be possessed by a particle. Moreover, all the particles do not have the same energy at any given moment. The term *energy-level* is ordinarily used to express the energy-value allowed to a particle. The particles having the lowest amount of energy are said to be in the *ground-level* or *zero level*. The subsequent levels increase by discrete amounts of energy ; thus level one, level two, etc. have energies ϵ_1, ϵ_2, ϵ_3 . . . etc. per particle in the respective energy-levels. For simplicity, let us assume that the energy-levels are all equally spaced and the energy-value in a given level differs from the preceding one by one quantum, ϵ (= $h\nu$), as in Fig. 5*l*.

Suppose the system contains four particles (which are *indistinguishable*) which share a total energy 5ϵ. This energy defines the overall state of the system. The possible ways of their distribution are given in the Fig. 5*l*. Since total energy = 5ϵ, hence the particles cannot remain in any level beyond the sixth. It is seen there are six possible arrangements or we may call them their microstates. There may occur innumerable interactions or encounters and energy-exchanges, but always there would be one of these configurations, restricted by the condition of total energy = 5ϵ. If the atoms are distinguishable, then there would be many more possible arrangements, as illustrated in the next example.

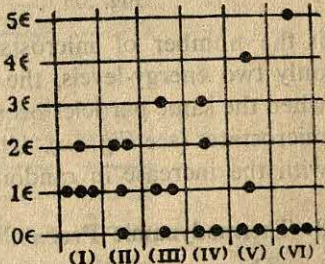

Fig. 5*l*

(*iv*) Let there be four *distinguishable* particles, *p*, *q*, *r* and *s* having a total energy 4ϵ. As such these particles may exist only up to the 5th energy-level. The different energy-levels which these four particles can possibly occupy are given in fig. 5*m*. The table shows that there are 5 possible patterns of distribution, *i.e.*, there are 5 macrostates subject to total energy value 4ϵ. The actual distribution of the particles in different macrostates is given in fig. 5*n*. There are 35 possible distributions. These are the total microstates. But the number of microstates is different for different macrostates. A *macrostate* is a description of how particles are present in different energy-levels. We cannot specify the microstate which exists at a given moment but nevertheless, they exist and are continuously changing with time We are not concerned with exact position or energy of the individual particles at any instant of time. Our aim is to find out the number of ways or arrangements in which the system can exist satisfying the condition of the macrostate.

Macrostates: 4 distriguistable particles with total energy 4ϵ

Energy Level	A	B	C	D	E
4		1			
3				1	
2			2		1
1	4			1	2
0		3	2	2	1
W	1	4	6	12	12

=35 Microstates

Fig. 5*m*

It will be easily seen from this example, the greater the number of energy-levels the particles occupy in a given macrostate, the larger is the number of microstates. When the four particles occupy only two energy-levels, the number of microstates is 4 or 6. But when the same particles occupy three energy levels, there are twelve microstates (see Fig. 5*n*). That is, the number of microstates increase with the increase in randomness of distribution.

B. Thermodynamic Probability

The number of microstates corresponding to a given macrostate is called its *thermodynamic probability*, denoted by W. The thermodynamic probability can never be less than one and will have very large values when the number of particles are large distributed amongst many energy-levels.

All microstates are equally probable but the most probable distribution is one having the maximum number of microstates, *i.e.*, having the most chaotic or randomised distribution. When the number is quite large, there is hardly any difference between the average distribution and the most probable distribution.

(*i*) *Computation of W*. The estimation of W is not difficult. Suppose a system has a collection of N particles (often called an *ensemble*). The energy distribution of the particles is described by the numbers $n_1, n_2, n_3, \ldots$ in the first, second, third . . . energy levels. Suppose that there are four particles to be accommodated in the ϵ_1-level (*i.e.*, $n_1 = 4$). Then, there are N-ways of choosing

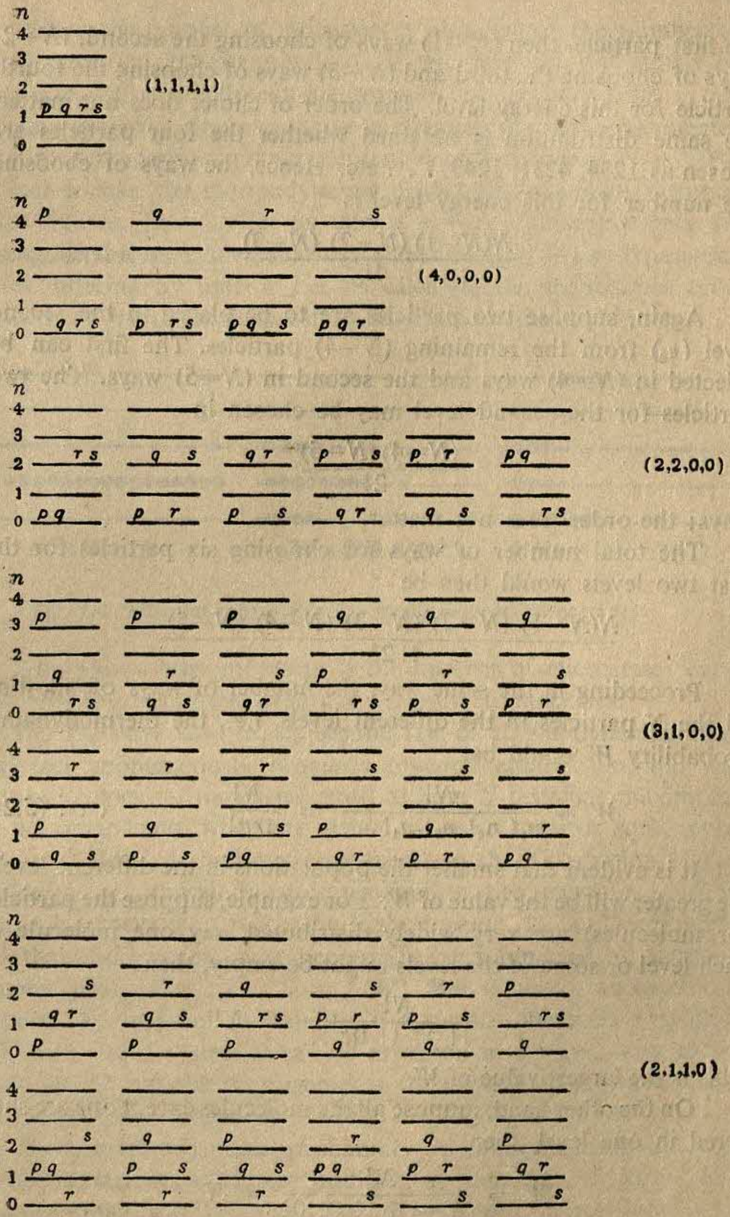

Fig. 5n

the first particle, then $(N-1)$ ways of choosing the second, $(N-2)$ ways of choosing the third and $(N-3)$ ways of choosing the fourth particle for this energy level. The order of choice does not matter, the same distribution is obtained whether the four particles are chosen as 1234, 4231, 1243, . . . etc. Hence, the ways of choosing the number for this energy level is

$$\frac{N(N-1)(N-2)(N-3)}{4!}$$

Again, suppose two particles are to be placed in the second level (ϵ_2) from the remaining $(N-4)$ particles. The first can be selected in $(N-4)$ ways and the second in $(N-5)$ ways. The two particles for the second level may be chosen in

$$\frac{(N-4)(N-5)}{2!}$$

ways; the order does not matter.

The total number of ways for choosing six particles for the first two levels would then be

$$\frac{N(N-1)(N-2)(N-3)(N-4)(N-5)}{4!\,2!}$$

Proceeding in the same way, the number of ways of allotting all the N particles in the different levels, *i.e.*, the thermodynamic probability W would be,

$$W = \frac{N!}{n_1!\,n_2!\,n_3!\,n_4!\ldots} = \frac{N!}{\Pi\, n!} \qquad \ldots (5.24)$$

It is evident that smaller the populations in the different levels, the greater will be the value of W. For example, suppose the particles (or molecules) are very widely distributed, say one molecule in each level or some of the levels might be empty, then

$$W = \frac{N!}{1!\,1!\,1!\,0!\,1!} = N!$$

This is the largest value of W.

On the other hand, suppose all the molecules except one are sheltered in one level, then

$$W = \frac{N!}{(N-1)!\,1!\,0!\,0!} = N$$

When N is large, $N! \gg N$. That is, thermodynamic probability is much higher with more random distribution.

When the number of molecules is quite small, the number of microstates, *i.e.*, the magnitude of W will be small and nearly of the same order in different macrostates, as we have seen in our previous examples. But when samples contain our usual experimental amounts, the number of molecules will be of the order of $N = 10^{20}$. In such a case, the thermodynamic probability would be astronomical figures. To wit : let us take a sample containing only 16 distinguishable molecules, sharing a total energy of 16ϵ and quantum states differing by unit ϵ. Let us calculate the microstates only in three of innumerable possible distributions, as in Fig. 5*p*.

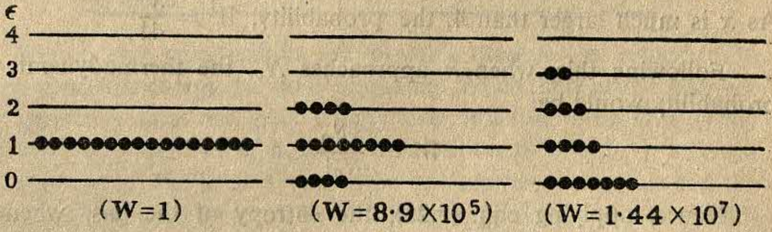

Fig. 5*p*. Defferent microstates fcr 16 distinguishable particles

This shows how enormous is the number of microstates even with only four quantum levels and for only 16 molecules.

(*ii*) We have seen in the second law of thermodynamics that a system spontaneously proceeds towards equilibrium and the entropy S goes on increasing until at eqm S becomes maximum. On the other hand, when the system proceeds towards eqm, more and more chaos or randomness appears in the distribution of the molecules, *i.e.*, thermodynamic probability also increases, and at eqm it is expected to reach the highest value. It can therefore be said that the entropy must necessarily be a function of thermodynamic probability ; *i.e.*, $S = f(W)$. But W is not an extensive property. In terms of probability, if a system A can be arranged in 3 ways and a system B can be arranged in 4 ways, then there would be 12 possible arrangements when both arrangements are considered simultananeously, *ie* $W_{tot} = W_A W_B$.

Thus, thermodynamic probability is multiplicative, but the entropy is extensive and hence, additive, so that $S_{tot} = S_A + S_B$. This prompted Boltzmann and Planck to suggest the relation,

$$S = k \ln W, \ (k = \text{Boltzmann constant}) \qquad \ldots (5.25)$$

This is indeed a postulate which can be justified.

(*iii*) Suppose a volume (V) of a gas contains N_o molecules. Imagine that the volume is divided into x cells in which molecules are distributed as in different energy levels. If the volume expands to V', the number of cells would increase to x' (say), such that $x'/x = V'/V$. With expansion in volume, the probability of distribution (W) shall also increase. To begin with, suppose there are only 4 molecules. To distribute them in x cells, the total possible choice would be $\frac{x(x-1)\,(x-2)\,(x-3)}{4!}$, the molecules being indistinguishable.

As x is much larger than 4, the probability, $W = \frac{x^4}{4!}$

Following this, when x approaches N_o, the thermodynamic probability would be

$$W = \frac{x^{N_o}}{N_o!}$$

Hence, applying eqn. (5.25), the entropy of the gas, when volume $= V_1$

$$S = k \ln W = k\,[N_o \ln x - \ln N_o\,!]$$

When the volume is increased to V' with x' cells in it, the entropy

$$S' = k \ln W' = k\;[N_o \ln x' - \ln N_o\,!]$$

$\therefore$ The change in entropy, $S' - S = k\,N_o \ln \frac{x'}{x}$

If $N_o =$ Avo. number, $\qquad \triangle S = R \ln \frac{V'}{V} \qquad \ldots (5.26)$

This is exactly the result obtained from classical considerations for the increase in entropy for the expansion of the system from volume V to V'. There is thus a justification for the postulate,

$$S = k \ln W$$

(*iv*) In expressing the thermodynamic probability (W) in the form of eqn. (5.24), it was tacitly assumed that the particles were distinguishable from each other, such as the atoms in a solid which are localised at specifiable points in a lattice. For indistinguishable particles as those in a gas, a different treatment is necessary. Moreover, the present ideas of quantum mechanics indicate that there are energy states which are distinct, though close, but of the same energy (value). For example, a particle having a velocity $C = \sqrt{51}$, *i.e.*, $C^2 = 51$, may have varied components of velocity C_x, C_y, C_z, in three perpendicular directions. To wit,

$C^2 = 51$

	I	II	III	IV	V	VI
C_x	7	1	1	5	5	1
C_y	1	7	1	5	1	5
C_z	1	1	7	1	5	5

That is, six complexions are possible though the velocity (C), and hence the energy, would be the same. When there exist a number of quantum states in a given energy level, it is said to be *degenerate*. If there be g number of possible distribution of energy in a given energy-level i, the level is said to be g_i degenerate ; g_i is called the statistical weight factor. The illustration given above is sixfold-degenerate ; the statistical weight factor is 6. The g_i-values may be different for different energy levels. The degeneracy does not alter the macrostates but increases the number of microstates enormously.

There is however a discrete number of energy levels for the molecules of a gas (indistinguishable). Our aim is to find how the molecules would be distributed in different energy levels at any moment. It can be shown from quantum mechanics that the number of quantum states g_i in any level i is much larger than the number of particles occupying that level. $g_i \gg n_i$,* and it can be presumed that it is unlikely that more than one molecule will occupy the same quantum state.

Due to incessant chaotic motion and rapid collisions, each molecule of a gas would undergo many changes from one quantum state to another.

---

*Suppose a monotomic ideal gas is enclosed in a cubical box of side a. At ordinary condition, the number of atoms per c.c. is about 2×10^{19}. From Schrödinger eqn, it can be shown that the possible number of energy states is given by $\phi = \frac{1}{8} \times \frac{4}{8} \pi \left(\frac{8ma^2\varepsilon}{h^2} \right)$ where m is the mass of each molecule having energy ε.

The velocity of the molecules at ordinary conditions is about 2.5×10^5 cm/sec, corresponding to an energy-value $\varepsilon \approx 10^{-13}$ ergs. For He, $m = 6.6 \times 10^{-24}$ gm. Substituting these values in the relation for ϕ, the number of quautun states is found to be 6×10^{25}. But there are 2×10^{19} atoms and hence there are more than million times more levels than the number of atoms. Therefore, at any instant, most of the quantum-levels would be empty, and in any level, only 1 atom would be found.

In a degenerate system, it can be visualised that every energy-level really constists of a bundle of levels. We denote the number of levels in the energy-levels *i.e.*, the i-th bundle by g_i having the mean energy ϵ_i. Then, there are,

n_1 particles in the 1st bundle of g_1-levels with energy ϵ_1
n_2 particles in the 2nd bundle of g_2-levels with energy ϵ_2
. . . .
n_i particles in the i-th bundle of g_i-levels with energy ϵ_i.
. . . .

The most probable values of n_i are those which would give the system maximum number of complexions.

Consider the i-th level having g_i-levels in it and n_i particles. If the particles were all distuiguishable, then the number of their distribution *i.e.*, complexions would be $g_i^{n_i}$ (see previous section). But in the case of indistinguishable particles, this number must be divided by the number of permutations of the particles amongst themselves, *i.e.*, by $n_i!$. Hence, the required number of micro-states or complexions for this level is

$$g_i^{n_i} / n_i\,!$$

Therefore, the total number of complexions, taking into consideration all the energy-levels, would be

$$W = \frac{g_1^{n_1}}{n_1!} \cdot \frac{g_2^{n_2}}{n_2!} \cdot \quad \ldots \frac{g_i^{n_i}}{n_i!}, \; \ldots = \Pi \, \frac{g_i^{n_i}}{n_i!} \qquad \ldots (5.27)$$

Exercises

1. Calculate the entropy change when

(*a*) two moles of an ideal gas are suddenly released into an evacuated vessel such that its pressure falls from 5/3 atm to 1 atm.

(*b*) two moles of oxygen (C_p = 6.095 cal/mole) are heated from 27°C to 127°C (*i*) at constant pressure and (*ii*) at constant volume.

(*c*) Argon contained in an insulated tank at 120°F and 40 psia. On opening a valve, the gas flows into an evacuated insulated tank of the same size.

Ans. (*a*) 2.044 *e.u.* (*b*) 3.505, 2.355 *e.u.* (*c*) 1.377 e.u./mole.

2. A copper block A (mass = 1 gm, temp 100°C) is brought in contact with another copper block B (mass = 3 gm, temp 300°C). They are allowed to come into thermal eqm. adiabatically. Determine the total entropy-change, (the specific heat of copper = 0.096 cal/gm°C). **Ans.** + 0.0063 e.u.

3. A two-kilowatt electric heater runs for 110 minutes attaining 827°C. The room-temperature is 27°C. What is the overall increase in entropy?

Ans. 3.2×10^4 $J/°K$.

4. A uniform metal bar composed of 2 moles is so treated that one half has a higher temp T_2 and the other half cooled to a lower temp T_1. The bar is suddenly enclosed in an insulated chamber. Show that the change in entropy

$$\triangle S = C_p ln \frac{(T_2 + T_1)^2}{4T_1T_2}$$

5. Calculate $\triangle U$, $\triangle H$ and $\triangle S$ when 1 mole of liquid water at 0°C and 1 atm is converted into steam at 200°C and 3 atm. Given $L_v = 9.7$ kcal/mole ; C_p (steam) $= 8.81 - 1.9 \times 10^{-3}T$. Assume ideal behaviour for steam.

Ans. $\triangle H = 12.3$ kcal, $\triangle U = 11.4$ kcal, $\triangle S = 31.4$ e.u.

6. At 25°C, the latent heat of vaporisation of ethyl alcohol is 10190 cal/mole and its vap. pressure is 59.0 mm. The liquid alcohol at 25°C has an entropy of 38.4 e.u. per mole. What will be the entropy of a mole of ethyl alcohol vapour, behaving ideally, at 25°C and 1 atm.? **Ans.** 67.5 e.u.

7. Given, for ammonia per gm.-mole

$C_p(l) = 17.9$ cal; $C_p(g) = 8.04 + 7 \times 10^{-4}T$ cal

$L_{vap} = 5560$ cal ; $B.pt = 239.7°K$

Calculate the entropy-change when 1 mole of liquid ammonia at const. pressure at −40°C is transformed into gaseous state at 200°C. **Ans.** 8.66 e.u.

8. The molar heat capacities for H_2O are

$$C_p(l) = 18.0 \text{ cal}, \; C_p(g) = 9.0 \text{ cal}$$

and the latent heat of vaporisation $L_{373} = 9713$ cal.

What will be the change in entropy when one mole of liquid water vaporises at constant pressure of 1 atm. and 25°C? **Ans.** 28.0 e.u.

9. One mole of Argon at 1 atm. and 25°C expands isothermally into a connecting evacuated cylinder of 10 litre capacity. Show that the change in entropy will be 0.68 e.u.

10. At 17°C and 1 atm., 800 c.c. of nitrogen were mixed with 200 c.c. of oxygen. Show that the change in entropy for mixing would be 0.0418 e.u.

11. There are nine quantum states for pure ortho-hydrogen at 0°K. All states being present in equal amounts, calculate the entropy of the mixture.

Ans. 4.36 e.u.

12. Calculate the change in entropy when 5 gm of water at 20°C is converted into saturated vapour at 100°C, assuming specific heat of water to remain constant and equal to unity and latent heat of vaporisation = 537 cal/gm.

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13. Establish:

$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

14. Calculate the entropy-changes at tne different steps of a reversible Carnot's cycle which takes up 1000 cal from the source at 400°K and releases 'q_2' calories to the sink at 300°K. Find also q_2. What is the net entropy change of the cycle? **Ans.** Step (1) = 2.50 e.u., $q_2 = 750$ cal

15. Evaluate ΔS for the following processes :

(*a*) $H_2O\ (l, -5°C) \longrightarrow H_2O\ (s, -5°C)$

(*b*) $H_2O\ (l, 1\ \text{atm}, 125°C) \longrightarrow H_2O\ (g, 1\ \text{atm}, 125°C)$

Given for one of mole of H_2O,

$L_v = 9713$ cal, $L_f = 1440$ cal

$C_{p_s} = 9$ cal, $C_{p_g} = 18$ cal ; vapour pressure at 125°C = 1740.5 mm.

Ans. (*a*) −5.11 e.u. (*b*) 25.4 e.u.

16. Calculate :

(*a*) the number of macrostates for four particles having a total energy of 6ϵ, the energy levels are equally spaced. **Ans.** 9

(*b*) What will be the thermodynamic probability when the four particles are distributed as one in each level? **Ans.** 24

(*c*) What will be the total no. of microstates? **Ans.** 84

17. Three distributions of 30 particles are given :

Energy level	P	Q	R
0	15	15	16
1	7	8	8
2	3	1	1
3	3	4	2
4	2	2	3

Find out which distribution is most probable.

18. An isolated system with 3 particles has a total energy $3h\nu$. The energy levels are equally spaced one unit apart, the ground level has zero energy. Find out the number of macrostates. How many microstates are possible if tne particles are distinguishable. **Ans.** 3, 10

19. Three distinguishable particles have a total energy of 9 units. But the particles are restricted to energy levels from 0 to 4. Calculate the number of macrostates and microstates. **Ans.** 3, 10

20. (*a*) Five quanta of energy are shared among 5 oscillators. What are the possible configurations and what would be the total number of microstates? **Ans.** 126

(*b*) Five quanta of energy are shared among 10 oscillators. Find out the total number of microstates. Which configuration will have the highest number of microstates? **Ans.** 2002

21. (*a*) A 20 c.c. sealed ampule containing 0.01 mole of a gas at very high pressure is kept suspended in an insulated 5-litre flask, completely evacuated. The ampule suddenly breaks and the gas fills up the flask. What will be the change in entropy, if any?

(*b*) A saturated *supercooled* solution of sodium thiosulphate is kept isolated in a Dewar flask and seeded with a tiny crystal. Spontaneous crystallisation occurs. Obviously this is accompanied with organisation of the molecules and hence entropy should decrease. How the crystallisation could be spontaneous?

22. (*a*) Show that in an isoentropic transformation of an ideal gas

$$\left(\frac{\partial V}{\partial T}\right)_s = -\frac{C_v}{C_p - C_v}\cdot\left(\frac{\partial V}{\partial T}\right)_p$$

(*b*) Show that

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x$$

23. In an adiabatic constant volume cylinder are kept 1 mole of ideal gas A and 1 mole of ideal gas B separated by a movable but non-permeable piston. The volumes initially occupied by A and B are V_A and V_B. The piston is slowly moved until eqm is attained, i.e. they are at equal pressures in equal volumes (T constant). Show that the entropy-change is,

$$\triangle S = R\ ln\,\frac{(V_A + V_B)^2}{4V_AV_B}$$

CHAPTER 6

FREE ENERGY FUNCTIONS

Entropy is of course an important tool in the thermodynamic study of changes in systems. The entropy-change, $dS = \delta q/T$, where δq is not a perfect differential. There may be increase in entropy in an irreversible process (say diffusion) even when $\delta q = 0$. In such cases, there are obvious difficulties. Of course, in an isolated system, entropy increases with spontaneous changes and reaches its maximum at equilibrium. But natural processes seldom occur in isolated condition ; the systems do interact with the surroundings. The precise estimation of the entropy-change in the surroundings is often quite inconvenient. It is necessary to develop criteria in which the changes in the given system may be followed without any reference to its interaction with the surroundings though it exists. For this purpose two new thermodynamic functions are introduced, which also utilise entropy in their derivation.

These two thermodynamic functions which are extensively used are:

(*i*) *Helmholtz free energy or Work function, A*

(*ii*) *Gibb's free energy, G.* This is often called *thermodynamic potential* or *Gibb's energy* or *simply, free energy.*

6.1. Work Function and Gibb's Free Energy

The two functions have been defined as

$$A = U - TS \quad \ldots (6.1)$$

$$G = H - TS \quad \ldots (6.2)$$

Since $q = T\triangle S = TS_2 - TS_1$; the product of temperature and entropy (TS) must be a quantity of energy and as such TS can be algebraically added to U or H.

Again, U, H, T and S are state properties, hence A and G will also be defined by the states of the system ; dA and dG will be exact differentials.

Again $H = U + PV$, therefore

$$G = H - TS = U + PV - TS \quad \ldots (6.3)$$

and also $G = A + PV \quad \ldots (6.4)$

Confusion in the Nomenclature: It is necessary to mention here the confusion that prevails in the literature of thermodynamics regarding the nomenclature of these two functions. The quantity '$U-TS$' has been called free energy by one school of writers, while '$H-TS$' has been named free energy by another school. In consequence the subsequent derivations have been most confusing as the symbol F has been used differently by different schools. We mention here some of the expressions and symbols in use.

	$U-TS$	$H-TS$
I	Work function, A	Free energy, F
II	Helmholtz function, A	Gibbs function, G
III	Free energy, F	Gibbs potential, G

To avoid any such confusion, we shall not use the symbol 'F' for any of the two functions. In this text, we shall use $A = U-TS$ and call it 'work function'. We shall use $G = H-TS$ and mention it as 'free-energy' or 'Gibbs' energy'.

6.2. Work function, A

$$A = U-TS$$

For an isothermal reversible change of the system, we have

$$\triangle A_T = \triangle U - T\triangle S \quad ; \qquad (\triangle T = 0)$$

$$= \triangle U - q = -w_{\max}$$

or

$$-\triangle A_T = w_{\max} \qquad \ldots (6.5)$$

where $w_{\max}$ is the reversible, hence maximum, work involved.

It may then be said that the *work function*, A is such a thermodynamic property of the system that its decrease gives the maximum amount of work available during an isothermal transformation of the system. This work may be purely mechanical or otherwise or may be partly mechanical and partly external.

It should however be remembered that (*i*) if the same transformation be irreversible then the same drop in A would occur but it would exceed the output of work, *i.e.*, $-\triangle A > w$.

(*ii*) if the change be not isothermal, the change in work function A will not be equivalent to the maximum work.

Again

$$A = U-TS$$

$\therefore$

$$dA = dU - TdS - SdT$$

or

$$dA = dU - q - SdT$$

or

$$dA = -PdV - SdT \qquad \ldots (6.6)$$

Then, for an isochoric process, $\left(\frac{\partial A}{\partial T}\right)_V = -S,$ . . . (6.7)

for an isothermal process, $\left(\frac{\partial A}{\partial V}\right)_T = -P$ . . . (6.8)

6.3. Free energy, *G*

$$G = H - TS$$

or $$G = U + PV - TS$$

If a system undergoes an isothermal reversible change at constant pressure, then

$$\triangle G = \triangle U + P\triangle V + V\triangle P - T\triangle S - S\triangle T$$

or $$\triangle G_{P,T} = \triangle U + P\triangle V - T\triangle S = \triangle U + P\triangle V - q$$

$$= P\triangle V - w_{\max}$$

or $$-\triangle G_{P,T} = w_{\max} - P\triangle V \qquad \text{. . . (6.9)}$$

where $P\triangle V$ is the mechanical work involved in the system itself during the transformation and $w_{\max}$ denotes the maximum total work output.

Hence $w - P\triangle V$ is the amount of work received for any external use, exclusive of the mechanical work in the change of the system itself.

Free energy (G) is thus a property of the system whose decrease is the measure of the external useful work available during the transformation of the system.

It should be remembered that the equality in eqn (6.9) holds true in an isothermal reversible process.

Again, $G = U + PV - TS$

hence, $dG = dU + PdV + VdP - TdS - SdT.$

For a reversible mechanical process, $dU + PdV = q = TdS$

So, $$dG = VdP - SdT \qquad \text{. . . (6.10)}$$

For an isobaric process, $\left(\frac{\partial G}{\partial T}\right)_P = -S$ . . . (6.11)

For an isothermal process, $\left(\frac{\partial G}{\partial P}\right)_T = V$ . . . (6.12)

Standard Value for G : *G* is a state function. To assign numerical values to free energy changes of a system, it is necessary to put a standard value for the free energy of the system at a specified state. As in the case of enthalpy and entropy, the standard state for free energy is usually taken as that at a constant temperature of 25°C and 1 atmosphere for a pure substance.

At const. temperature (T), the free energy at any pressure (P) can be easily expressed with the help of eqn (6.12).

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad , \quad \text{or} \quad \int_1^{\Pi} dG = \int_1^{P} VdP$$

$$\text{or} \qquad G - G^\circ = \int_1^{P} VdP \ ,$$

where G° is the standard free energy of the system at 1 atm and the same temperature.

$$\therefore \qquad G = G^\circ + \int_1^{P} VdP \qquad \ldots (6.13)$$

If the system contains n moles of a perfect gas at T°K, then,

$$G = G^\circ + \int_1^{P} \frac{nRT}{P} dP = G^\circ + nRT \, ln \, \frac{P \text{ atm}}{1 \text{ atm}}$$

$$\text{or} \qquad G = G^\circ + nRT \, ln \, P \qquad \ldots (6.14)$$

$$\text{or} \qquad G/n = G^\circ/n + RT \, ln \, P \qquad \ldots (6.15)$$

$$i.e., \qquad \bar{G} = \bar{G}^\circ + RT \, ln \, P \qquad \ldots (6.16)$$

where $\bar{G}$, $\bar{G}^\circ$, are corresponding free-energies for 1 mole of the gas.

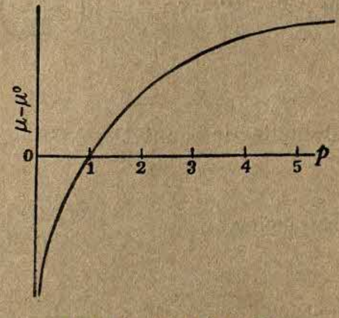

Fig. 6a. $\mu - \mu^\circ$ vs P

Usually the free-energy of a gm-molecule of a substance is nowadays expressed by the symbol, μ. That is,

$$\bar{G} = G/n = \mu \qquad \ldots (6.17)$$

$\therefore$ From eqn (6.16),

$$\mu = \mu^\circ + RT \, ln \, P \quad \ldots (6.18)$$

Evidently, the free energy increases with increase in pressure. A plot of $(\mu-\mu^\circ)$ versus P is given in fig $6a$. The significance of μ will be discussed in detail in a later chapter.

6.4. Effect of Temperature on Free Energy. Gibbs-Helmholtz Equations

From eqns (6.7) and (6.11),

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

(*a*) Now $A = U - TS$ and $G = H-TS$

$$\text{or} \quad A = U + T\left(\frac{\partial A}{\partial T}\right)_V \text{ and } G = H + T\left(\frac{\partial G}{\partial T}\right)_P \quad \ldots (6.19)$$

This pair of equations are called *Gibbs-Helmholtz equations*. Re-arranging,

$$\left(\frac{\partial A}{\partial T}\right)_V = \frac{A-U}{T} \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = \frac{G-H}{T} \quad \ldots (6.20)$$

These equations may also be given other forms.

(*b*) In an *isothermal change*, we have

$$G_1 = H_1-TS_1 \quad \text{and} \quad G_2 = H_2-TS_2$$

The suffix 1 for initial state and 2 for final state of the system.

Subtracting, $\triangle G = \triangle H-T\triangle S$ . . . (6.21)

$$\text{But } \triangle S = (S_2-S_1) = -\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right] = -\left(\frac{\partial(\triangle G)}{\partial T}\right)_P \quad \ldots (6.22)$$

$$\text{Substituting in eqn (6.21), } \triangle G = \triangle H + T\left(\frac{\partial(\triangle G)}{\partial T}\right)_P \quad \ldots (6.23)$$

$$\text{Rearranging,} \quad \left[\frac{\partial(\triangle G)}{\partial T}\right]_P = \frac{\triangle G-\triangle H}{T} \quad \ldots (6.24)$$

$$\text{Similarly,} \quad \left[\frac{\partial(\triangle A)}{\partial T}\right]_V = \frac{\triangle A-\triangle U}{T} \quad \ldots (6.25)$$

(*c*) Sometimes it is more useful to find the differential of G/T with respect to temperature.

We know $$\left[\frac{\partial}{\partial T}(G/T)\right]_P = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P - G\frac{1}{T^2}$$

$$= -\frac{S}{T} - \frac{G}{T^2} = -\frac{G+TS}{T^2}, \text{(from 6.11)}$$

or $$\left[\frac{\partial(G/T)}{\partial T}\right]_P = -\frac{H}{T^2} \qquad \ldots (6.26)$$

Likewise, $$\left[\frac{\partial(A/T)}{\partial T}\right]_V = -\frac{U}{T^2} \qquad \ldots (6.27)$$

(d) Since $d(1/T) = -\frac{1}{T^2}\,dT$, we can write eqn (6.26) as;

$$\left[\frac{\partial(G/T)}{\partial(1/T)}\right]_P = H \qquad \ldots (6.28)$$

and so, $$\left[\frac{\partial(A/T)}{\partial(1/T)}\right]_V = U \qquad \ldots (6.29)$$

These are the different forms of the well-known Gibbs-Helmholtz relations [eqns 6.19, 6.20, 6.23, 6.26, and 6.28]. These relations are extensively used in thermodynamic consideration of various phenomena, such as phase changes, chemical equilibria, emf of voltaic cells, surface energy, etc.

Problem : The latent heat of fusion of ice at 0°C = 1440 cal and the heat capacities of ice and water are 8.7 and 18 calories per mol. Calculate the change in Gibbs potential in the freezing of a mole of water at −20°C.

From Kirchhoff's equation:

$$\triangle H = \triangle H_0 + \int_0^{273} \triangle Cp dT = \triangle H_0 + \int_0^{273} -9.3\ dT$$

$$\text{or} \quad \triangle H_0 = \triangle H - \int_0^{273} -9.3\ dT$$

$$= -1440 + 9.3 \times 273 = 1099$$

$$\text{or} \quad \triangle H = 1099 - 9.3T$$

Following eqn (6.26), $$\frac{\triangle G}{T} = -\int \frac{\triangle H}{T^2}\,dT = -\int \frac{\triangle H_0 - 9.3T}{T^2}\,dT$$

$$= \frac{1099}{T} + 9.3 \ln T + Z \text{ (constant)}$$

$$\text{or} \quad \triangle G = 1099 + 9.3T \ln T + ZT$$

We know at 0°C, ice and water are in equilibrium, $\triangle G_{273} = 0$

Hence, $\triangle G_{273} = 1099 + 9.3 \times 273 \ln 273 + Z \times 273 = 0$

whence, $Z = -56.$

Therefore, $\triangle G$ at -20°C is

$\triangle G_{253} = 1099 + 9.3 \times 253 \ln 253 - 56 \times 253 = -69$ cal/mole

6.5. A mathematical Interlude

If f be a function of two variables x, y; then the total differential is

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

The two differential coefficients $\partial f/\partial x$ and $\partial f/\partial y$ are functions of x, y. Let us say,

$$\left(\frac{\partial f}{\partial x}\right)_y = M_{(x,y)} \text{ and } \left(\frac{\partial f}{\partial y}\right)_x = N_{(x,y)} \qquad \ldots (i)$$

Hence, $df = Mdx + Ndy$

From (i), $\dfrac{\partial^2 f}{\partial y \partial x} = \dfrac{\partial M}{\partial y}$ and $\dfrac{\partial^2 f}{\partial x \partial y} = \dfrac{\partial N}{\partial x}$

But it has been shown earlier that for a perfect differential,

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}$$

Hence, $$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad \ldots (ii)$$

These are often called *cross derivatives* of the relation,

$$df = Mdx + Ndy$$

To illustrate : We know, $dU = TdS - PdV$

So from (ii), $\left(\dfrac{\partial T}{\partial V}\right)_S = -\left(\dfrac{\partial P}{\partial S}\right)_V$

6.6. Maxwell's Relations

We have come across four fundamental thermodynamic relations. These are :

(1) $dU = TdS - PdV$

(2) $dH = TdS + VdP$

$$(3)\quad dA = -PdV - SdT$$

$$(4)\quad dG = VdP - SdT$$

Exercising the cross-derivative rule, we have

$$\left.\begin{aligned}
&(i) && \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \\
&(ii) && \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \\
&(iii) && \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \\
&(iv) && \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T
\end{aligned}\right\}\quad \ldots (6.30)$$

The equations tabled in 6.30 called *Maxwell's relations* are very useful in dealing with various physico-chemical phenomena.

Again, from (1) above, $\left(\frac{\partial U}{\partial S}\right)_V = T$

and from (2) above, $\left(\frac{\partial H}{\partial S}\right)_P = T$

Hence, $\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P$

Thus, from the said relations (1), (2), (3) and (4), we have,

$$\left.\begin{aligned}
&\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T ;\ \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial A}{\partial P}\right)_T \\
&\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P
\end{aligned}\right\}\quad \ldots (6.31)$$

To illustrate a simple use of Maxwell relation, the determination of entropy-change due to variation of pressure may be mentioned.

From eqn (6.30), $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)$

Rearranging, $\Delta S = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP$, ($T$, constant)

The change in entropy due to change in pressure at constant temperature for any system can be computed from this, as $\left(\frac{\partial V}{\partial T}\right)_P$ is easily measurable.

If the system be one of an ideal gas (1 mole),

then $\Delta S = -\int_{P_1}^{P_2} \frac{R}{P} dP = R \ln \frac{P_1}{P_2}$, [See Eqn 5.18]

The deviation of entropy due to non-ideality of the gas :

Suppose one mole of an ideal gas is compressed from a very low pressure P_0 (Lt $P_0 \rightarrow 0$) to a pressure of 1 atm, then

$$\Delta S_{id} = S^*_1 - S^*_{P_0} = -\int_{P_0}^{1} \frac{R}{P} dP \qquad \ldots (i)$$

* asterisk indicates ideality of the gas.

Now suppose, the same is done with one mole of a real gas, say Berthelot gas, then

$$\Delta S = S_1 - S_{P_0} = -\int_{P_0}^{1} \left(\frac{\partial V}{\partial T}\right)_P dP$$

For a Berthelot gas, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{27}{32} \cdot \frac{RT_c^3}{P_c T^3}$

$$\text{So, } \Delta S_{\text{real}} = S_1 - S_{P_0} = -\int_{P_0}^{1} \left[\frac{R}{P} + \frac{27}{32} \cdot \frac{RT_c^3}{P_c T^3}\right] dP \qquad \ldots (ii)$$

Now at low pressures, a real gas behaves also ideally, hence $S^*_{P_0} = S_{P_0}$. Hence subtracting (*ii*) from (*i*), we have

$$S^*_1 - S_1 = \int_{P_0}^{1} \frac{27}{32} \cdot \frac{RT_c^3}{P_c T^3} \cdot dP$$

$$= \frac{27}{32} \cdot \frac{RT_c^3}{P_c T^3}, \quad \text{since } P_0 \text{ is too small.}$$

This gives the deviation in entropy.

6-7. Standard Free Energy

The absolute free energy of a substance cannot be experimentally determined. Since in thermodynamic solutions we are concerned with free energy *changes* only, so it is sufficient if some arbitrary standard be fixed to compute the free energy. As in the case of enthalpy, the free energy of an *element* in its stable form at 25°C and 1 atm has, by convention, been assigned the value 'zero'.

The free energy of a compound is the change in free energy which occurs during its formation from its constituent elements. Hence, for a compound,

$$G^\circ = \triangle G^\circ_f \text{ (free energy of formation).}$$

For example, the standard free energy change during the formation of one mole of water ($\triangle G^\circ_f$) is -54.64 Kcal.

$$\begin{array}{lllll} & H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g) \ ; & & \triangle G^\circ_f = -54.64 \text{ Kcal} \\ G^\circ \rightarrow & 0 \quad\ \ 0 \qquad\quad x & & \end{array}$$

$$\text{Now } \triangle G^\circ_f = x - 0 - 0 = x \ ; \ \therefore G^\circ_{H_2O} = x = -54.64 \text{ Kcal}$$

That is, the free energy G° of a mole of $H_2O(g)$ is the same as its free energy of formation.

The standard free energy change of a process can then be computed from the standard free energy of formation of the resultants and the reactants ; it will be the difference of the $\triangle G^\circ_f$ values of the resultants and the reactants. In the reaction,

$$pA + qB = rC + sD$$

$$\begin{aligned} \triangle G^\circ_{\text{reaction}} &= r\triangle G^\circ_{f(C)} + s\triangle G^\circ_{f(D)} - p\triangle G^\circ_{f(A)} - q\triangle G^\circ_{f(B)} \\ &= \Sigma\triangle G^\circ_{f(\text{products})} - \Sigma\triangle G^\circ_{f(\text{reactants})} \quad \ldots (6.32) \end{aligned}$$

The standard free energy of formation of a few compounds are tabulated here.

TABLE : STANDARD FREE ENERGY OF FORMATION $\triangle G^\circ_f$ AT 25°C (KCAL/MOLE)

Gases	$\triangle G^\circ_f$	*Liquids*	$\triangle G^\circ_f$
H_2O	-54.64	H_2O	-56.69
N_2O	24.9	CH_3OH	-39.73
NO	20.7	C_2H_5OH	-41.77
NO_2	12.4	CH_3COOH	-93.8
NH_3	-3.97	C_6H_6	29.76
CO	-32.80		
CO_2	-94.26	Solids	
HCl	-22.77		
SO_2	-71.80	CuO	-30.4
SO_3	-88.5	Cu_2O	-35.0
H_2S	-7.88	Fe_2O_3	-177.1
		Al_2O_3	-376.8
CH_4	-12.14	$CaCO_3$	-269.8
C_2H_6	-7.86	$CaSO_4$	-315.6
C_3H_8	-5.61	$BaSO_4$	-350.2
$C_4H_{10}(n)$	-3.75	$BaCO_3$	-272.2
$C_4H_{10}(iso)$	-4.3	$AgCl$	-26.2
C_2H_2	50.0	$AgBr$	-22.9
C_2H_4	16.28	$NaCl$	-91.9

Problem : Estimate the standard free energy change of the chemical reaction,

$$CO + H_2O = CO_2 + H_2$$

using necessary data from the table.

	CO	H_2O	CO_2	H_2	
$\Delta G^\circ_f \rightarrow$	-32.8	-54.64	-94.26	0	Kcal

$$\therefore \ \Delta G^\circ = -94.26 + 0 - (-32.8) - (-54.64) = -6.8 \text{ Kcal}$$

6.8. Spontaneity and Equilibrium

I. At one time, it was intuitively assumed that a spontaneous change occurs only when it would lead to a lowering of the energy value of the system. The apple falls from a tree or the glaciers run down hill for the gravitational energy is lowered; a water drop takes a spherical shape as it would reduce surface area and hence surface energy ; a candle burns in air as the change is accompanied with expulsion of heat energy, etc. It is true that in many spontaneous processes decrease in energy of the system is involved. But this is not universally true. There are instances in which ΔH or ΔU of the system may be zero or may be positive, and yet the change is spontaneous.

A gas freely expands into an evacuated vessel (Joule's expt). This is a spontaneous process involving no heat-change. There is something other than energy (increase of randomness) which is responsible for the spontaneity.

The decomposition of $AgClO_2$ (s) at a slightly warm condition occurs spontaneously practically without any heat of reaction ;

$$AgClO_2(s) \rightarrow Ag(s) + O_2(g) + \tfrac{1}{2}Cl_2(g) \ ; \quad \Delta H \approx 0$$

Here again, it occurs due to increase in randomness.

On the other hand, spontaneous evaporation of highly volatile liquids like ether takes place with absorption of heat and hence with increase in energy, ΔH is positive.

Endothermic chemical reactions, like the hydrolysis of thionyl chloride, show that the spontaneous processes are accompanied with ΔH as positive.

$$SO_2Cl_2(l) + H_2O(l) = SO_2(g) + 2HCl(g) \ ; \quad \Delta H = +50 \text{ kJ}$$

The assertion that spontaneity is accompanied with attainment of minimum energy level is not tenable.

II. In the preceding chapter, we have seen that in a reversible change the net entropy remains unaltered, whereas in a spontaneous, and hence irreversible, change the net entropy increases. If dS and dS' represent the entropy-changes of the system and the surroundings respectively, then

(*a*) for a reversible change, $dS + dS' = 0$

(*b*) for an irreversible change, $dS + dS' > 0$

Combining the two, $dS + dS' \geqslant 0$

Suppose a system undergoes an isothermal but irreversible change and let dU and w be the internal energy change and work. Suppose further that the surroundings supply q heat reversibly to the system, such that $dS' = -q/T$.

Now $$dS + dS' \geqslant 0$$

or $$dS - \frac{q}{T} \geqslant 0$$

or $$dS - \frac{dU + w}{T} \geqslant 0, \quad \text{(from the 1st Law)}$$

or $$TdS - dU - w \geqslant 0$$

or $$TdS - dU - PdV \geqslant 0 \qquad \ldots (6.33)$$

assuming the work is mechanical, ($w = PdV$).

Remember the symbols in the eqn (6.33) refer to the system only.

For a reversible process, $TdS - dU - PdV = 0$

and for a real process to occur in nature, $TdS - dU - PdV > 0$

For a change at constant U and V,

$$dS_{U,V} \geqslant 0$$

At eqm, S becomes maximum, $dS_{U,V} = 0$

The condition for a process to occur in nature,

$$dS_{U,V} > 0 \qquad \ldots (6.34)$$

III. The possibility of a process occurring is more clearly assessed by considering the free energy change of the system only instead of enthalpy or entropy.

We know,

$$dG = dU + PdV + VdP - SdT - TdS$$

or $$TdS - dU - PdV = -dG + VdP - SdT$$

Hence from eqn (6.33), $-dG + VdP - SdT \geqslant 0$

or $dG \leqslant VdP - SdT$

From eqn (6.10), we know, for a reversible change

$$dG = VdP - SdT$$

Hence for any spontaneous *irreversible change*

$$dG < VdP - SdT$$

or at constant P and T, $dG_{P,T} < 0$ . . . (6.35)

For a *reversible change*, $dG_{P,T} = 0$

It must be remembered, whenever a system is in eqm, G reaches its minimum, and $dG = 0$.

$\therefore$ at equilibrium, $VdP - SdT = 0$ . . . (6.36)

The same criteria would apply to both physical and chemical transformations.

The possibility of a chemical change.

For a process taking place from a given initial to a given final state, $\triangle U$ would be the same. From the 1st Law,

(*a*) for reversible occurrence, $q_{\text{rev}} = \triangle U + w_{\text{rev}}$

(*b*) for irreversible occurrence, $q_{\text{irrev}} = \triangle U + w_{\text{irrev}}$

But we know, $w_{\text{rev}} > w_{\text{irrev}}$; hence $q_{\text{rev}} > q_{\text{irrev}}$

Therefore, for an infinitesimal change, $dq_{\text{irrev}} - dq_{\text{rev}} < 0$. . . (*A*)

By definition $G = U + PV - TS$

or
$$\begin{aligned} dG &= dU + PdV + VdP - TdS - SdT \\ &= q + VdP - TdS - SdT \end{aligned}$$

the work is supposed to be purely mechanical.

Chemical reactions are carried out usually at a fixed temperature and pressure, therefore

$$dG_{P,T} = q - TdS$$

for a spontaneous hence irreversible process

$$\begin{aligned} dG_{P,T} &= q_{\text{irrev}} - TdS \\ &= q_{\text{irrev}} - q_{\text{rev}} \quad [\text{for } dS = q_{\text{rev}/T}] \end{aligned}$$

Hence, from (*A*), $dG_{P,T} < 0$.

That is, in a spontaneous change, $\triangle G$ must be negative.

To find out if a given process would be spontaneous at a specified T and P, we have only to calculate $\triangle G$ of the system alone. If $\triangle G$ is *negative*, the change shall spontaneously occur. If $\triangle G$ is *zero*, the initial and final states would exist at eqm with each other. If $\triangle G$ is *positive*, the process will not occur spontaneously, but its reverse may.

6.9. Evaluation of the free energy change

The enthalpy-change ($\triangle H$) can be determined from calorimetric measurements. In a chemical process, $\triangle H$ can also be evaluated from bond-energies of the resultants and reactants. $\triangle H$ is also available from the temperature coefficients of eqm constants (see Reaction Isochore).

The entropy (S) of a substance can be evaluated at a given pressure and temperature with the help of the third law. The entropy-change ($\triangle S$) is obtained by subtracting the entropy of the reactants from that of the resultants. Thus in a reaction,

$$A + B = C$$

the entropy-change $\triangle S = S_C - S_A - S_B$,

where S-terms are the individual entropies of the different entities. Sometimes, $\triangle S$ is also obtained from other sources such as emf measurement.

Now, the free-energy change ($\triangle G$) for an isothermal process,

$$\triangle G = \triangle H - T\triangle S$$

The value of $\triangle H$ and $\triangle S$ can be ascertained by methods noted above. Hence, the magnitude of $\triangle G$ is easily known. If $\triangle G$ is found negative, the process contemplated is favoured.

The variation of $\triangle H$ and $\triangle S$ with temperature is not large. Hence for approximate calculations, $\triangle H$ and $\triangle S$ determined at a convenient temperature may be used for reactions at other temperatures without an appreciable error. But the change in free-energy ($\triangle G$) varies considerably with temperature.

If $\triangle H$ be negative and $\triangle S$ be positive, we have negative values for $\triangle G$. Such a process will always be spontaneous. When $\triangle H$ is negative and $\triangle S$ is also negative, the process will be spontaneous only when $\triangle H$ is numerically greater than $T\triangle S$.

In endothermic reactions, $\triangle H$ is positive. The reaction shall occur if $T\triangle S$ is positive and greater than $\triangle H$.

$\triangle G$ can also be evaluated from other sources, such as from emf measurements, from equilibrium constants, etc. These will be considered in subsequent chapters.

Some illustrative examples are given below :

Example : At 1 atm and 27°C, will the vaporisation of liquid water be spontaneous? Given $\triangle H = 9710$ cal and $\triangle S = 26$ e.u.

$$H_2O(l) = H_2O(g), \qquad (P = 1 \text{ atm})$$

$$\triangle G = \triangle H - T\triangle S = 9710 - 26 \times 300 = +1910 \text{ cal}$$

Since $\triangle G$ is positive, at 1 atm, vaporisation is not possible. Rather the reverse process of condensation will occur.

∴ The temperature at which the liquid and vapour will be in eqm can be obtained, by putting $\triangle G = 0$; *i.e.*,

$$\triangle G = 9710-26T = 0$$
$$T = 373.4°\text{K}$$

This indeed is the boiling pt. of water at 1 atm.

Example : For the process,

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2 \quad ; \quad \triangle H = -20000 \text{ cal}$$

and $\triangle S = 18$ e.u.

Will the reaction be spontaneous at 25°C?

$$\triangle G = \triangle H - T\triangle S = -20000 - 298 \times 18 = -25364 \text{ cal}$$

The dissociation will be spontaneous.

Example : In the endothermic reaction,

$$C + H_2O(g) \rightarrow CO(g) + H_2(g); \quad \triangle H = +31400 \text{ cal}$$

and $\triangle S = +32$ e.u.

Discuss the feasibility of the reaction at 100°C and 1000°C.

$$\triangle G_{373} = 31400 - 32 \times 373 = +19464 \text{ cal}$$
$$\triangle G_{1273} = 31400 - 32 \times 1273 = -9336 \text{ cal}$$

The reaction would not take place at 100°C but shall spontaneously proceed at 1000°C.

Example : In the formation of water at 25°C and 1 atm,

$$H_2 + \tfrac{1}{2}O_2 = H_2O(l); \quad \triangle H = -68320 \text{ cal}$$
$$S° \rightarrow 31.21 \quad \tfrac{1}{2}(49) \quad 16.71$$

Show that the process is spontaneous.

$$\triangle S = 16.71 - 31.21 - \tfrac{1}{2}(49) = -39 \text{ e.u.}$$
$$\therefore \quad \triangle G = \triangle H - T\triangle S = -68320 + 298 \times 39 = -56698 \text{ cal}$$

Since $\triangle G$ is negative, it is thermodynamically predicted that formation of water would proceed spontaneously. But a mixture of H_2 and O_2 does not seem to react appreciably at 25°C. This is because of the extremely slow rate of reaction, which is not a concern of thermodynamics. If the rate be accelerated by a catalyst or a spark, the eqm will be established easily.

A transformation which is not favoured at a given temperature and pressure may be achieved by suitably altering the pressure, temperature remaining constant. This may be illustrated by examples given below :

Example : The molar entropy and volume of graphite and diamond at 298°K and 1 atm are :

	S° (cal)	V° (c.c.)
graphite	1.37	5.3
diamond	0.58	3.4

The heats of combustion of graphite and diamond are:

$$(a)\ C_{gra} + O_2 \rightarrow CO_2; \qquad \triangle H^\circ = -94030 \text{ cal}$$

$$(b)\ C_{dia} + O_2 \rightarrow CO_2\ ; \qquad \triangle H^\circ = -94480 \text{ cal}$$

(*i*) Show that graphite is the more stable form of carbon at 298°K and 1 atm. (*ii*) Find out the pressure at which graphite would acquire the tendency to be transformed into diamond.

(*i*) Subtracting (*b*) from (*a*) above

$$C_{gra} \rightarrow C_{dia}\ ; \qquad \triangle H^\circ = +\ 450 \text{ cal}$$

$$\therefore\ \triangle G^\circ = \triangle H^\circ - T\triangle S^\circ$$

$$= 450 - 298\,(0.58 - 1.37) = +\ 685 \text{ cal}$$

Since $\triangle G^\circ$ is positive, the proposed change would not occur, so graphite is more stable than diamond.

(*ii*) $$\triangle G = VdP - SdT$$

At const. T, $$\triangle G_T = VdP$$

or $$\partial(\triangle G) = (V_2 - V_1)dP$$

Now for the proposed transformation

$$\triangle G^\circ = +\ 685 \text{ cal} = 685 \times 41.3 \text{ cc-atm} = 28.3 \text{ lit-atm}$$

$$V_2 - V_1 = (3.4 - 5.3) = -1.9 \text{ cc} = -0.0019 \text{ litre}$$

Temperature remaining constant (298°K), suppose at pressure P, graphite would be in eqm with diamond, when $\triangle G_P = 0$.

At 1 atm (298°K), $$\triangle G^\circ = 28.3 \text{ lit-atm.}$$

$\therefore$ $$\int_{28.3}^{o} \partial(\triangle G) = \triangle V \int_{1}^{P} dP$$

i.e. $$-28.3 = -\ 0.0019\ (P-1)$$

whence $$P = 14896 \text{ atm.}$$

That is, it is thermodynamically predicted that at about 15000 atm pressure graphite is capable of being transformed to diamond ($T = 298°K$). That such a possibility exsits is proved from the fact that minute crystals of diamond have been obtained from graphite under a pressure of 75000 atm at about 1500°K.

Example: The two forms of $CaCO_3$ are *calcite* and *aragonite*. Their thermodynamic data per mole at 25°C and 1 atm are

	$H°$(Kcal)	$S°$ (cal)	$V°$(cc)
calcite	−288.45	22.2	36.90
aragonite	−288.49	21.2	33.93

(*i*) Is calcite more stable than aragonite at 25°C? (*ii*) Find out the pressure at which calcite and aragonite would be in eqm at 25°C.

(*i*) At 25°C and 1 atm, for calcite → aragonite

$$\Delta H° = H_2° - H_1° = -40 \text{ cal } [= -40(41.3) \text{ cc-atm/°K}]$$

$$\Delta S° = S_2° - S_1° = -1.0 \text{ cal } [= -41.3 \text{ cc-atm/°K}]$$

$$\Delta V° = V_2° - V_1° = -2.97 \text{ c.c.}$$

The suffix 1 stands for calcite, suffix 2 for aragonite.

For the proposed change, $\Delta G° = \Delta H° - T\Delta S°$

$$= -40 - 298(-1) = +258 \text{ cal}$$

Since $\Delta G°$ is positive, calcite will not be transformed into aragonite at 1 atm and 25°C.

(*ii*) Suppose under a pressure P atm, the two forms would be in eqm at the constant temp T (298°K). At the point of eqm, $\Delta G = 0$; i.e., $G_1 = G_2$

$$\therefore \quad U_1 + PV_1 - TS_1 = U_2 + PV_2 - TS_2$$

$$\text{or} \quad P(V_2 - V_1) = T(S_2 - S_1) - (U_2 - U_1)$$

$$\text{or} \quad P = T\frac{\Delta S}{\Delta V} - \frac{\Delta U}{\Delta V} = T\frac{\Delta S}{\Delta V} - \frac{\Delta H}{\Delta V},$$

since for solid transformations, $\Delta U \approx \Delta H$.

$$\therefore \quad P = T\frac{-41.3}{-2.97} - \frac{(-40)(41.3)}{-2.97}$$

$$= 13.9\,T - 556$$

$$= 13.9 \times 298 - 556 = 3596 \text{ atm}$$

6.10. Free Energy of gases

We have seen in eqn 6.18 that for a gm-mole of an ideal gas, at temp. T,

$$\mu = \mu^\circ + RT \ln P$$

where μ, μ° are the molar free energies at P atm and 1 atm.

If the system changes from pressure P_1 to P_2, then

$$\Delta \bar{G} = \mu_2 - \mu_1 = RT \ln (P_2/P_1) \qquad \ldots (6.37)$$

But if the system contains a *real* gas (say, a van der Waals gas), where $\bar{V} \approx \frac{RT}{P} + (b - a/RT)$, the evaluation of the integral $\int \bar{V} dp$ is not simple. From eqn. (6.13),

$$\mu = \mu^\circ + \int_1^P \bar{V} dP = \mu^\circ + \int_1^P [RT/P + (b - a/RT)] dP$$

Now, $(b - a/RT) = B$, the second virial coefficient of the virial equation for gases. Then,

$$\mu = \mu^\circ + \int_1^P \left(\frac{RT}{P} + B \right) dP = \mu^\circ + RT \ln P + B(P-1)$$

Hence $\Delta \bar{G} = \mu_2 - \mu_1 = RT \ln P_2/P_1 + B(P_2 - P_1) \ldots (6.38)$

Example : Calculate the change in molar free energy of N_2 at 27°C when it expands from 5 atm to 1 atm, as (*i*) an ideal gas and (*ii*) van der Waals gas. Given $b = 0.039$ lit and $a = 1.35$ lit-atm units.

(*i*) As an ideal gas :

$$\Delta \bar{G} = RT \ln P_2/P_1 = 2 \times 300 \times 2.303 \log (1/5) = -966 \text{ cal}$$

(*ii*) As a van der Waals' gas :

$$B = b - a/RT = 0.039 - \frac{1.35}{0.082 \times 300} = -0.016 \text{ litres}$$

$$\therefore \ \overline{\Delta G} = RT \ln (1/5) + (-0.016)(1-5)(2/.082) \text{ cal}$$
$$= -966 + 1.56 = -964.44 \text{ cal}$$

6.11. Free energy change in mixing of gases

At a constant temperature under a pressure P, the molar free energy of a pure ideal gas i is

$$\mu_i^* = \mu_i^\circ + RT \ln P$$

Under the same total pressure if this gas be present mixed with other gases and its partial pressure be p_i, then its molar free energy μ_i will be

$$\begin{aligned} \mu_i &= \mu_i^\circ + RT \ln p_i \\ &= \mu_i^\circ + RT \ln x_i P, \quad (\because\ p_i/P = x_i \text{ mol-fraction}) \\ &= \mu_i^\circ + RT \ln P + RT \ln x_i \\ &= \mu_i^* + RT \ln x_i \qquad \ldots (6.39) \end{aligned}$$

the * asterisk indicates the pure state of the susbtance.

Suppose at a constant temperature and under the same pressure, n_1, n_2, n_3 . . . moles of different gases are mixed when their initial molar free energies are μ_1^*, μ_2^*, μ_3^*, . . . After mixing, let the molar free energies be given by μ_1, μ_2, μ_3, etc. Since free energy is an extensive property, hence

$$G_{\text{initial}} = n_1\mu_1^* + n_2\mu_2^* + n_3\mu_3^* + \ldots$$

$$G_{\text{on mixing}} = n_1\mu_1 + n_2\mu_2 + n_3\mu_3 + \ldots$$

$$\therefore\ \Delta G_{\text{mixing}} = n_1(\mu_1 - \mu_1^*) + n_2(\mu_2 - \mu_2^*) + n_3(\mu_3 - \mu_3^*) + \ldots$$

Uusing equation, 6.39,

$$\Delta G_{\text{mixing}} = n_1\, RT \ln x_1 + n_2\, RT \ln x_2 + n_3\, RT \ln x_3 + \ldots$$

where x_1, x_2, x_3 . . . are the mol-fractions of the different components.

$$\Delta G_{\text{mixing}} = n\, RT\, [(n_1/n) \ln x_1 + (n_2/n) \ln x_2 + (n_3/n) \ln x_3 + \ldots]$$

where $n_1 + n_2 + n_3 + \ldots = n$, total moles in the mixture.

$$\Delta G_{\text{mixing}} = n\, RT \Sigma\, x_i \ln x_i \qquad \ldots (6.42)$$

This gives the free energy decrease in mixing ideal gases. When only two ideal gases are mixed,

$$\begin{aligned} \Delta G &= n\, RT\, [x_1 \ln x_1 + x_2 \ln x_2] \\ &= n\, RT\, [x_1 \ln x_1 + (1 - x_1) \ln (1 - x_1)] \end{aligned}$$

When ΔG is potted against x_1 from this relation, a curve as in Fig. 6.6 with a minimum is obtained. The free energy decrease is largest at the minimum point.

$$\therefore\ \frac{d(\Delta G)}{dx_1} = 0.$$ Solving, it is found at the minimum point, $x_1 = \frac{1}{2}$.

That is, free energy decrease will be largest when equimolar quantities of the two components are mixed.

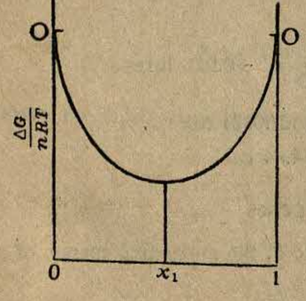

Fig. 6.*b*

6.12. Variation of $\triangle G$ with P and T

At the standard state, $\triangle G^\circ = \triangle H^\circ - T\triangle S^\circ$ . . . (*i*)

and at any pressure P and temp. T, $\triangle G = \triangle H - T\triangle S$ . . . (*ii*)

The superscript zero represents the standard condition, $P = 1$ atm, $T = 298$°K.

$$\text{Now} \left[\frac{\partial(\triangle H)}{\partial T}\right]_P = \triangle C_P\text{ , hence } \triangle H_T = \triangle H^\circ + \int_{298}^{T} \triangle C_P\, dT$$

$$\text{Again} \left[\frac{\partial(\triangle S)}{\partial T}\right]_P = \frac{\triangle C_P}{T}\text{, hence } \triangle S_T = \triangle S^\circ + \int_{298}^{T} \frac{\triangle C_P\, dT}{T}$$

$$= \triangle S^\circ + \int_{298}^{T} \triangle C_P\, d\ln T$$

Substituting these in the eqn (*ii*),

$$\triangle G = \triangle H^\circ + \int_{298}^{T} \triangle C_P\, dT - T\triangle S^\circ - T\int_{298}^{T} \triangle C_P\, d\ln T$$

$$= \triangle G^\circ + \int_{298}^{T} \triangle C_P\, dT - T\int_{298}^{T} \triangle C_P\, d\ln T \quad . . . (iii)$$

The eqn (*iii*) gives the value of $\triangle G$ when temperature is changed to T, the pressure ($P = 1$ atm) remaining constant.

From eqn. (6.10), it is easily seen,

$$\left[\frac{\partial(\triangle G)}{\partial P}\right]_T = \triangle V\text{ , hence } \triangle G = \int_{1}^{P} (\triangle V) dP$$

This gives the *variation* in $\triangle G$ purely for change in pressure at a constant temperature.

Hence the general expression for free energy-change should be

$$\triangle G = \triangle G^\circ + \int_{298}^{T} \triangle C_P\, dT - T\int_{298}^{T} \triangle C_P\, d\ln T + \int_{1}^{P} (\triangle V)\, dP \quad . . . (6.42)$$

The three integrals on the rt-hand side can be obtained from experimental measurements, hence the change of $\triangle G$ from the standard value ($\triangle G^\circ$) can be ascertained.

6.13. Excess Thermodynamic Functions

The free energy change in the mixing of two pure substances (Sec. 6-11) for 1 mole of the mixture or solution.

$$\triangle G^i_{mix} = RTx_1 \ln x_1 + RTx_2 \ln x_2 \quad \ldots (A)$$

This relation is valid for an ideal mixture or solution. In real systems, the free energy change of mixing (say, $\triangle G'_{mix}$) usually differs from $\triangle G^i_{mix}$. The difference between $\triangle G'_{mix}$ for non-ideal mixtures and $\triangle G^i_{mix}$ for ideal mixtures has been defined as *excess free energy of mixing* denoted by $\triangle G^E$. Hence

$$\triangle G^E = \triangle G'_{mix} - \triangle G^i_{mix} \quad \ldots (B)$$

The superscript 'i' is used for ideal and the stroke (′) is used for nonideal mixtures.

Such differences in other thermodynamic properties for real and ideal mixtures also arise when two pure substances are mixed.

The difference between the thermodynamic function of mixing for a real system and that for an ideal system, temperature and pressure remaining constant, is called 'excess thermodynamic function'. Thus if ϕ denotes any thermodynamic property, then excess ϕ in mixing is given by

$$\phi^E = \phi'_{mix} - \phi^i_{mix}$$

Expressions for some thermodynamic functions may be deduced as follows :

(*i*) *Excess free energy*, $\triangle G^E$. For the free energy change in mixing forming non-ideal systems, the activity function may be used, so that

$$\begin{aligned}\triangle G'_{mix} &= RT\,x_1 \ln a_1 + RT\,x_2 \ln a_2, \text{ (per mole of mixture)}\\ &= RT\,x_1 \ln x_1\gamma_1 + RT\,x_2 \ln x_2\gamma_2\\ &= RT\,x_1 \ln x_1 + RT\,x_1 \ln\gamma_1 + RTx_2 \ln x_2 + RTx_2 \ln\gamma_2 \quad \ldots (C)\end{aligned}$$

Then from eqns (A), (B) and (C),

$$\triangle G^E = \triangle G'_{mix} - \triangle G^i_{mix} = RTx_1 \ln\gamma_1 + RTx_2 \ln\gamma_2 \quad \ldots (D)$$

(*ii*) *Excess entropy function*, $\triangle S^E$. By definition, excess entropy of mixing,

$$\begin{aligned}\triangle S^E &= \triangle S'_{mix} - \triangle S^i_{mix}\\ &= -\left(\frac{\partial(\triangle G)^E}{\partial T}\right)_P\\ &= -RTx_1\frac{d\ln\gamma_1}{dT} - RTx_2\frac{dn\gamma_2}{dT} - Rx_1\ln\gamma_1 - Rx_2\ln\gamma_2 \quad \ldots (E)\end{aligned}$$

(*iii*) *Excess enthalpy function*, $\triangle H^E$

$$\triangle H^E = \triangle H'_{mix} - \triangle H^i_{mix}$$

But $\triangle H^E = \triangle G^E_{mix} + T\triangle S^E_{mix}$

Multiply eqn (E) by T and add eqn (D),

$$\triangle H^E = -RT^2\left[x_1\frac{d\,ln\gamma_1}{dT} + x_2\frac{d\,ln\gamma_2}{dT}\right] \quad \ldots \text{(F)}$$

For an ideal mixture, $\triangle H^i_{mix} = 0$, hence

$$\triangle H^E = \triangle H'_{mix} \quad , \text{ (non-ideal mixtures)}$$

If γ_1, γ_2 be independent of temperature, then $(\partial ln\ \gamma/\partial T)$ would be zero ; hence $\triangle H^E = 0$. Therefore, enthalpy change $\triangle H'_{mix}$ even for a non-ideal mixing *may be* zero. That is, $\triangle H_{mix} = 0$, does not necessarily prove the ideality of a mixture.

(*iv*) *Excess volume in mixing*, $\triangle V^E$

$$\triangle V^E = [\triangle G^E/\partial P]_T$$

$$\text{[from(D)]} \qquad = RT\left[x_1\frac{\partial ln\gamma_1}{\partial P} + x_2\frac{\partial ln\gamma_2}{\partial P}\right] \quad \ldots \text{(G)}$$

It is thus seen that the different thermodynamic excess functions are related to the activity coefficients of the components of the mixture. A determination of the vapour pressures of the solute and the solvent would enable the computation of the excess functions.

Problems

1. Calculate W, $\triangle U$, $\triangle S$, $\triangle A$ and $\triangle G$ for the following processes :

(*a*) 10 gm He (ideal gas) expands isothermally and reversibly at 0°C from 100 atm to 10 atm.

(*b*) One mole of steam condenses reversibly to water at 100°C and 1 atm [$l = 539.4$ cal/gm].

Ans. (*a*) $w = -\triangle A = -\triangle G = 3125$ cal ; $\triangle U = 0$; $\triangle S = 11.25$ e.u.

(*b*) $w = -\triangle A = -740$ cal; $\triangle G = 0$; $\triangle U = -8970$ cal, $\triangle S = -26$ e.u.

2. The standard free-energy of ammonia at 25°C is −3976 cal/mole. Find the values of molar free energy at ½ atm and at 10 atm at 25°C.

Ans. −4387 cal ; −2611 cal

3. Calculate the free energy change in mixing 3 moles of hydrogen with 1 mole of nitrogen at 25°C. **Ans.** −1338 cal

4. Three moles of Helium, behaving ideally, expand from 5 litres to 25 litres at 127°C. Calculate $\triangle G$. Ans. -3864 cal.

5. At 50°C, the eqm pressure of water vapour over a mixture of $CuSO_4(s)$ and $CuSO_4, H_2O(s)$ is 4.5 mm. Evaluate $\triangle G$ for the process,

$$CuSO_4, H_2O(s) = CuSO_4(s) + H_2O(g), \text{ when } P = 1 \text{ atm.}$$

Ans. $\triangle G = +3290$ cal

6. In the reaction,

$$N_2 + O_2 \rightarrow 2NO; \ \triangle H = +43.2 \text{ Kcal},$$

the change in entropy is 5.9 cal/degree. Calculate the free energy change at 1000°C and discuss the feasibility of the process.

7. Calculate standard thermodynamic potential changes to find out if

(*a*) metallic aluminium will reduce, CuO, ZnO, CaO

(*b*) gaseous hydrogen will reduce CuO, BaO, AgCl (Use tables)

8. For the reaction,

$$2Hg(l) + Cl_2(g) \rightarrow Hg_2Cl_2 \ ; \ \triangle H^\circ_{298} = -264.3 \text{ kj}$$

From the emf of a voltaic cell involving this reaction, $\triangle G^\circ_{298}$ is found to be -205.2 kj. Calculate the standard change in entropy for this process.

Ans. -192j/°K

9. At 25°C, the entropies of white tin and grey tin are 6.30 and 6.16 e.u respectively

$$Sn_{white} \rightarrow Sn_{grey} \ ; \ \triangle H^\circ_{298} = 0.53 \text{ Kcal}$$

which modification of tin is stable at 25°C?

10. At a temperature of -5°C, solid benzene has a vapour pressure of 19.8 mm and supercooled liquid benzene 17.1 mm. Calculate the free energy change of solidification of supercooled benzene (1 mole) at -5°C. Assume ideal behaviour.

[Hints : Visualise the transformation reversibly ; (*a*) vaporise reversibly 1 mole supercooled benzene liquid at -5°C and $P = 17.1$ mm. (*b*) change reversibly 1 mole vapour from $P = 17.1$ mm. to $P = 19.8$ mm. at -5°C. (*c*) Condense reversibly at -5°C to solid state at constant pressure.] Ans. -326j

11. Derive the relations :

(*i*) $$\left(\frac{\partial T}{\partial P}\right)_s = \frac{T}{C_P}\left[\frac{\partial V}{\partial T}\right]_p$$

(*ii*) $$\left(\frac{\partial H}{\partial V}\right)_T = -V^2\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial (T/V)}{\partial V}\right)_p$$

(*iii*) $$\left(\frac{\partial G/T}{\partial 1/T}\right)_p = H$$

12. Show that

(*i*) $$\left(\frac{\partial P}{\partial T}\right)_s = \frac{\gamma}{\gamma - 1}\left(\frac{\partial P}{\partial T}\right)_v$$

(*ii*) $$\left(\frac{\partial V}{\partial T}\right)_s = \frac{\gamma}{1-\gamma}\left(\frac{\partial V}{\partial T}\right)_p$$

13. Calculate the standard $\triangle G^\circ_{298}$ for the reaction,

$$Cu_2O + NO(g) \rightarrow 2CuO + \tfrac{1}{2}N_2(g)$$

Given standard free energy of formation for Cu_2O, CuO and NO as $-35.2, -30.4$ and $+ 20.7$ Kcal respectively. **Ans.** -46.3 Kcal

14. Calculate the change in thermodynamic potential in the reaction, at standard conditions,

(*a*) $CaCO_3 \rightarrow CaO + CO_2$

(*b*) $Zn + Cu^{++} \rightarrow Cu + Zn^{++}$

15. The red HgO is fairly stable. Its standard thermodynamic potential of formation is given by

$$\triangle G^\circ_{HgO(f)} = -21600 + 26.4T$$

Discuss its stability at 500°K and 850°K.

16. The free energy change in the stretching of a water film (at const T and P) is given by $\triangle G = 75.64 - 0.14t$ (ergs) where t is the temperature in °C. Calculate $\triangle U$, $\triangle S$ and $\triangle A$, when the film area is increased reversibly by 1 sq. cm. at 10°C.
Ans. $\triangle U = 113.8$ ergs ; $\triangle S = 0.14$ ergs/°K ; $\triangle A = 74.24$ ergs

17. Calculate the change in free energy at 25°C for

$$Br_2(l) = Br_2 \text{ (aq. solution, conc. } = 0.01 \text{ m)}$$

Given, at 25°C, the vapour pressure of pure $Br_2 = 0.28$ atm. The vapour pressure of bromine in aqueous solution is given by $p = 1.45x$, where x is the molality.
Ans. -7345 joules/mole

18. Suppose air is an ideal gas with mol. wt. 29 and the earth's atmosphere is isothermal at 0°C. At what height in meters the pressure would be 0.5 atm?

[Note : $G = \psi(T) + RT\,ln\,P + Mgh$, at height h. Establish $P = P_0 e^{-Mgh/RT}$]

19. One mole of CO_2 a van der Waals gas expands from 3 atm to 1 atm at 27°C. Find out $\triangle G$ and $\triangle A$. [Given $a = 3.61$ l^2-atm-mole^{-2} and $b = 42.8$ cc-mole^{-1}.] **Ans.** $\triangle G = -650$ cal, $\triangle A = -655$ cal

20. Show that $dS = \dfrac{C_V}{T}\left(\dfrac{\partial T}{\partial P}\right)_V dP + \dfrac{C_P}{T}\left(\dfrac{\partial T}{\partial V}\right)_P dV$

and deduce from it the adiabatic relation, $PV^\gamma =$ const, for an ideal gas.

Also show that $TdS = C_V \left(\dfrac{\partial T}{\partial P}\right)_V \left[dP - \gamma \left(\dfrac{\partial P}{\partial V}\right)_T dV \right]$

21. The reaction : $Ag + \tfrac{1}{2}Hg_2Cl_2 \rightarrow AgCl + Hg$

The following data are given in calories per mole :

	S^0	$\triangle G^0{}_f$	$\triangle H^0{}_f$
Ag	10.21	0.0	0.0
Hg_2Cl_2	46.8	-50350	-63320
AgCl	22.97	-26220	-30360
Hg	18.50	0.0	0.0

Is the reaction endothermic and yet spontaneous at 25°C? Explain.

CHAPTER 7

SOME USEFUL THERMODYNAMIC RELATIONS

7.1. Equations for change of Entropy

The coefficients of expansion and compressibility are given in sec 1-9 as,

Coeff. of expansion, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, or $\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$ . . . (a)

and coeff. of compressibility, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$, or $\left(\frac{\partial V}{\partial P}\right)_T = -\beta V$ . . . (b)

Further, from these relations, (see sec. 1-9). $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$ or $\left(\frac{\partial T}{\partial P}\right)_V = \frac{\beta}{\alpha}$ . . . (c)

(*i*) To find an expression for dS in terms of V and T, we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

(from Maxwell relations) $= \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$ . . . (7.1)

or $dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV$, [from (c) above] . . . (7.2)

Also, $\left(\frac{\partial S}{\partial V}\right)_T = \alpha/\beta$ . . . (7.2*a*)

(*ii*) But it will be more useful to express dS in terms of P and T,

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

(from Maxwell relations) $= \frac{C_P dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$ . . . (7.3) or $$dS = \frac{C_p dT}{T} - \alpha V dP \qquad \text{[from (a) above]} \qquad \ldots (7.4)$$

Also $$\left(\frac{\partial S}{\partial P}\right)_T = \alpha V \qquad \ldots (7.4a)$$

(*iii*) Using the parameters *P* and *V*, the expression for *dS* would be,

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

$$= \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$= \frac{C_V}{T} \cdot \left(\frac{\partial T}{\partial P}\right)_V dP + \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)_P dV$$

$$= \frac{C_V}{T} \cdot \frac{\beta}{\alpha} dP + \frac{C_P}{T} \cdot \frac{1}{\alpha V} dV \qquad \ldots (7.5)$$

The change in entropy can thus be evaluated from experimental measurements of heat-capacities and coefficients of expansion and compressibilities.

Example : Calculate the amount of heat liberated when one mol of copper is compressed isothermally and reversibly at 0°C from one atmosphere to 5000 atmospheres. (Given : Coefficient of expansion = 5×10^{-5} and molar volume = 7.06).

By the second *TdS*-equation, $TdS = C_P dT - \alpha VTdP$, (eqn. 7.4)
Since the process is isothermal,

$$q = T\triangle S = -\alpha VT\triangle P$$

$$= -\alpha VT(P_f - P_i)$$

$$= \frac{-5\times10^{-5}\times7.06\,(\text{cc})\times273\times(5000-1)\times1.013\times10^{6}}{4.2\times10^{7}}$$

$$= -11.62 \text{ cal}$$

Example : What would be the rise in temperature when 1 cc of water at 10°C is reversibly and adiabatically compressed from 0 to 1000 atmospheres?

$$[\alpha = 1.5\times10^{-5},\ C_P = 1.005]$$

we have, $$0 = TdS = C_P dT - \alpha VTdP$$

or $$\triangle T = \frac{\alpha VT}{C_P}\triangle P$$

$$= \frac{1.5\times10^{-5}\times1.0\times283\times1000\times1.013\times10^{6}}{1.005\times4.2\times10^{7}} = 0.1019°\text{C}$$

7.2. Equation for the change in Internal Energy and Enthalpy

(*i*) $$dU = TdS - PdV$$

Substituting dS from equation (7.1),

$$dU = T\left[C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV \right] - PdV$$

$$= C_V\, dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] dV \qquad \ldots (7.6)$$

Hence, at constant temperature

$$\left(\frac{\partial U}{\partial V}\right)_T = \left[T\left(\frac{\partial P}{\partial T}\right)_V - P \right] \qquad \ldots (7.7)$$

Again, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$, hence,

$$dU = C_V dT + \left[\frac{T\alpha}{\beta} - P \right] dV \qquad \ldots (7.8)$$

(*ii*) Again, $dU = TdS - PdV$
Substituting dS from equation (7.3),

$$dU = T\left[C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \right] - PdV \qquad \ldots (7.9)$$

But $$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Substituting dV in eqn (7.9), we have.

$$dU = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP - P\left(\frac{\partial V}{\partial T}\right)_P dT - P\left(\frac{\partial V}{\partial P}\right)_T dP$$

$$= \left[C_P - P\left(\frac{\partial V}{\partial T}\right)_P \right] dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T \right] dP$$

$$= [\, C_P - P\alpha V \,]\, dT - [\, T\alpha V - P\beta V \,]\, dP \qquad \ldots (7.10)$$

Further, from equation (7.8), $$\left(\frac{\partial U}{\partial V}\right)_T = T(\alpha/\beta) - P \qquad \ldots (7.11)$$

and from equation (7.10), $$\left(\frac{\partial U}{\partial P}\right)_T = P\beta V - T\alpha V \qquad \ldots (7.12)$$

The change in enthalpy can also be derived in a similar fashion.

(*iii*) $$dH = TdS + VdP$$

Substituting dS from equaion (7.3),

$$dH = T\left[C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP\right] + VdP$$

or $$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$\therefore \quad \left(\frac{\partial H}{\partial P}\right)_T = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] \qquad \ldots (7.13)$$

or $$\left(\frac{\partial H}{\partial P}\right)_T = V - \alpha VT \qquad \ldots (7.14)$$

Equations (7.7) and (7.13), namely,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

and $$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

are very useful. This pair of equations are called the fundamental thermodynamic equations of state. These are applicable to all systems.

(*iv*) Let us consider one mole of an ideal gas, $PV = RT$.

$$\therefore \quad (\partial P/\partial T)_V = R/V$$

So $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T.\frac{R}{V} - P = 0$$

The internal energy of an ideal gas is independent of volume, and hence also of pressure.

Again $$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = V - \frac{RT}{P} = 0$$

The enthalpy of an ideal gas is independent of pressure, and hence also of volume (see sec 2.6).

For a real gas, say van der Waals gas,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

Hence, $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{V-b} - P = \frac{a}{V^2}$$

(cf. sec 2.6*a*)

(*v*) Expressions for isothermal and adiabatic work can also be easily framed. Suppose the system is a solid.

The work in a reversible process ; $w = \int PdV$.

Now $$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$= -\beta VdP + \alpha VdT$$

For an isothermal process ; $w = \int -\beta VPdP$

$$= -\beta V\int PdP = -\frac{\beta V}{2}(P_2^2-P_1^2) \qquad \ldots (7.15)$$

assuming β and V remain constant for the solid.

For a reversible adiabatic process, $(dS = 0)$; $w = \int PdV$.

We know from equation (7.4), $dS = C_P\frac{dT}{T} - \alpha VdP$

But $dS = 0$, hence $dT = \frac{T\alpha V}{C_P}dP$

Now $V = f(S, P)$ $\therefore dV = \left(\frac{\partial V}{\partial S}\right)_P dS + \left(\frac{\partial V}{\partial P}\right)_S dP$

when $dS = 0$, $dV = \left(\frac{\partial V}{\partial P}\right)_S dP$

But the adiabatic compressibility, $\beta_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

$$\therefore \qquad dV = -\beta_S VdP$$

So work, $$w = \int PdV = -\beta_S V\int PdP$$

$$= -\beta_S V\left(\frac{P_2^2-P_1^2}{2}\right) \qquad \ldots (7.16)$$

HEAT CAPACITY RELATIONS

(*i*) C_V with V

we know, $C_V = \left(\frac{\delta q_r}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$, or, $\left(\frac{\partial C_V}{\partial V}\right) = T\frac{\partial^2 S}{\partial T \partial V}$

From Maxwell relations,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \quad \text{or,} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{\partial^2 S}{\partial V \partial T}$$

Hence, $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ . . . (7.17)

For an ideal gas ; $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$, and $\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$

$$\therefore \quad \left(\frac{\partial C_V}{\partial V}\right)_T \text{ (ideal gas)} = 0$$

For a real gas (van der Waals), $\left(P + \frac{a}{V^2}\right)(V-b) = RT$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}, \text{ and } \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

For a real gas, therefore, $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$

(*ii*) C_P with P.

We know, $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$, $\therefore$ $\left(\frac{\partial C_P}{\partial P}\right) = T\frac{\partial^2 S}{\partial T \partial P}$

From Maxwell's relations, $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$,

or, $$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\frac{\partial^2 S}{\partial P \partial T}$$

$$\therefore \quad \left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad \text{. . . (7.18)}$$

For an ideal gas $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$, $\quad\therefore\quad \left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$

$$\therefore \quad \left(\frac{\partial C_P}{\partial P}\right)_T \text{ (ideal gas)} = 0$$

For a real gas (van der Waals), $RT \approx PV - Pb + \frac{a}{V}$

$$\therefore \quad RdT = PdV - \frac{a}{V^2}\,dV, \qquad \text{at constant pressure.}$$

$$\therefore \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2}}$$

$$\text{Then, } \left[\frac{\partial^2 V}{\partial T^2}\right]_P = -\frac{R}{\left[P - \frac{a}{V^2}\right]^2} \times \frac{2a}{V^3} \times \left(\frac{\partial V}{\partial T}\right)_P$$

$$= -\frac{R}{\left[P - \frac{a}{V^2}\right]^2} \times \frac{2a}{V^3} \times \frac{R}{\left[P - \frac{a}{V^2}\right]}$$

$$= -\frac{2aR^2}{\left[P - \frac{a}{V^2}\right]^3 V^3} = -\frac{2aR^2}{P^3V^3\left[1 - \frac{a}{PV^2}\right]^3}$$

$$\approx -\frac{2aR^2}{R^3T^3\left[1 - \frac{a}{RTV}\right]^3} = -\frac{2a}{RT^3}\left[1 + \frac{3a}{RTV}\right]$$

Neglecting the second term, on first approximation,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \frac{2a}{RT^2} \qquad \ldots (7.19)$$

Example : What would be the change in the C_P-value of oxygen when at 27°C, its pressure is increased from zero to 50 atmospheres, supposing it behaves as a van der Waals' gas. Given $a = 1.36$ litre²-atm.

$$C_P - C_{P_0} = \triangle C_P = \int_0^P \frac{2a}{RT^2}\,dP = \frac{2a}{RT^2}P$$

$$= \frac{2 \times 1.36 \times 50}{(0.082) \times 300^2} \times 24.2 = 0.44 \text{ cal/degree-mole}$$

(1 litre-atm = 24.2 cal)

Example : How would the C_P of carbon-monoxide, which obeys Berthelot's equation, change when its pressure is raised from zero to 100 atmospheres at 27°C. Given P_c = 35 atmospheres and T_c = 135°K.

$$\text{Berthelot equation : } PV = RT\left(1 + \frac{9}{128}\frac{PT_c}{TP_c}\left[1 - \frac{6T_c^2}{T^2}\right]\right)$$

$$\text{or,} \qquad V = \frac{RT}{P} + \frac{9}{128}\frac{RT_c}{P_c} - \frac{54}{128}\frac{RT_c^3}{P_cT^2}$$

$$\text{or,} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{27}{32}\frac{RT_c^3}{P_cT^3}\ ; \text{ So, } \left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\frac{81}{32}\frac{RT_c^3}{P_cT^4}$$

$$\text{Now, } C_P - C_{P_0} = \triangle C_P = -T\int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right)_P dP = T\int_0^P \frac{81}{32}\frac{RT_c^3}{P_cT^4}.dP$$

$$= \frac{81}{32}\frac{RTc^3}{P_cT^3}P$$

$$= \frac{81 \times 0.082 \times (135)^3 \times 100 \times 24.2}{32 \times 35 \times 300^3}$$

$$= 1.307 \text{ cal/degree-mole}$$

7.4. Difference of heat capacities : $C_P - C_V$

Some equations expressing $(C_P - C_V)$ have already been given in Sec 2-8. There are others of easy application and interest ; these are mentioned here.

(*a*) Since, $S = f(T, V)$

$$\therefore \qquad dS = \left(\frac{\partial S}{\partial V}\right)_T dV + \left(\frac{\partial S}{\partial T}\right)_V dT$$

$$\text{or} \qquad TdS = T\left(\frac{\partial S}{\partial V}\right)_T dV + T\left(\frac{\partial S}{\partial T}\right)_V dT$$

$$\text{or, } T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\text{or,} \qquad C_P = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + C_V$$

$$\text{Hence, } \quad C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots (7.20)$$

Applying Maxwell relations, we have

$$C_P - C_V = -T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial S}{\partial P}\right)_T \qquad \ldots (7.21)$$

$$\text{also, } C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots (7.22)$$

Since $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ are usually positive, C_P is greater than C_V in any system. At absolute zero, however, $C_P = C_V$.

Also, when $\left(\frac{\partial V}{\partial T}\right)_P \to 0$, as in water at 4°C, $C_P \to C_V$.

$$\text{Again} \quad \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$\text{or} \quad \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

Substituting in eqn. (7.22), $C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2$

$$\ldots (7.23)$$

Rewriting we also have

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \Big/ \left(\frac{\partial V}{\partial P}\right)_T$$

$$= -T\,\frac{\frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P^2}{\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{-T\alpha^2}{-\beta/V} = \frac{\alpha^2 VT}{\beta} \qquad \ldots (7.24)$$

This relation is particularly useful for dealing with condensed systems.

Problem : Find out $(C_P - C_V)$ value of decane at 27°C, given molar volume 106 cc, the coefficient of expansion $\alpha = 1 \times 10^{-3}$ and coefficient of compressibility $\beta = 106 \times 10^{-6}\ \text{atm}^{-1}$

$$C_P - C_V = \frac{\alpha^2 VT}{\beta} = \frac{(1 \times 10^{-3})^2 \times 106 \times 300}{106 \times 10^{-6}}\ \text{cc-atm.}$$

$$= 300 \times 0.0242 = 7.26 \text{ calories}$$

Rewriting equation (7.24), we have

$$C_P - C_V = \frac{\alpha^2 VT}{\beta} = \left(\frac{\alpha^2 V}{\beta C_P{}^2}\right) C_P{}^2 T$$

It has been found empirically, for solids at low temperature, the term within the paranthesis is constant, *i.e.*,

$$\left(\frac{\alpha^2 V}{\beta C^2{}_P}\right) = A \text{ (constant)}$$

$$\therefore\ C_P - C_V = AC^2{}_P T$$

This is known as *Nernst-Lindemann equation* and is extensively used for determination of C_V of solids at low temperatures, which otherwise is difficult to measure.

(*i*) In an ideal gas, $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$, and $\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = T\frac{R}{V}.\frac{R}{P} = R$$

(*ii*) In a van der Waals' gas, $\left(P + \frac{a}{V^2}\right) = \frac{RT}{V-b}$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2}} \text{ (vide Sec. 7.3)}$$

Hence, $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = T\frac{R}{V-b}.\frac{R}{P-\frac{a}{V^2}}$

$$= \frac{RT}{V-b}.\frac{R}{\left(P + \frac{a}{V^2}\right) - \frac{2a}{V^2}} = \frac{RT}{V-b}.\frac{R}{\frac{RT}{V-b} - \frac{2a}{V^2}}$$

$$= \frac{RT}{V-b}.\frac{R}{\frac{RT}{V-b}\left[1 - \frac{2a(V-b)}{RTV^2}\right]}$$

$$= R\left[1 + \frac{2a(V-b)}{RTV^2}\right] \approx R\left[1 + \frac{2a}{RTV}\right]$$

$$= R\left[1 + \frac{2aP}{R^2T^2}\right] \qquad \ldots (7.25)$$

In general, the equation of state of a real gas up to the second virial (for moderate pressures) is

$$PV = RT + BP$$

i.e.,
$$P = \frac{RT}{V} + \frac{BP}{V} \approx \frac{RT}{V} + \frac{BRT}{V^2} \qquad \ldots (7.26)$$

In van der Waals', $PV \approx RT + \left(b - \frac{a}{RT}\right)P$

$$\therefore\ B = \left(b - \frac{a}{RT}\right); \qquad \frac{dB}{dT} = \frac{a}{RT^2}$$

In Berthelot's, $PV = RT + \frac{9}{128}\frac{RT_c}{P_c}\left(1 - \frac{6T_c^2}{T^2}\right)P$

$$\therefore \qquad B = \frac{9}{128}\frac{RT_c}{P_c}\left(1 - \frac{6T_c^2}{T^2}\right)$$

$$\therefore \qquad \frac{dB}{dT} = \frac{27}{32}\cdot\frac{RT_c^3}{P_cT^3}$$

From equation (7.26),

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} + \frac{BR}{V^2} + \frac{RT}{V^2}\left(\frac{dB}{dT}\right) \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{dB}{dT}$$

and

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{2R}{V^2}\cdot\frac{dB}{dT} + \frac{RT}{V^2}\cdot\frac{d^2B}{dT^2} \qquad \left(\frac{\partial^2 V}{\partial T^2}\right)_P = \frac{d^2B}{dT^2}$$

From eqn. (7.18),

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P; \qquad \left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Integrating between pressure zero and P, or between volumes ∞ and V, we can write

$$C_P - C_{P=0} = -T\int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right)_P dP = -T\int_0^P \frac{d^2B}{dT^2}\,dP$$

$$= -T\frac{d^2B}{dT^2}P$$

$$C_V - C_{V=\infty} = T\int_\infty^V \left(\frac{\partial^2 P}{\partial T^2}\right)_V dV = T\int_\infty^V \left(\frac{RT}{V^2}\cdot\frac{d^2B}{dT^2} + \frac{2R}{V^2}\cdot\frac{dB}{dT}\right)dV$$

$$\left(\because\ P = \frac{RT}{V}\right) \qquad = -T\frac{\partial^2 B}{dT^2}P - 2\frac{dB}{dT}P$$

Subtracting,

$$C_P - C_V = C_{P=0} - C_{V=\infty} + 2\frac{dB}{dT}P = R + 2\frac{dB}{dT}P \qquad \ldots (7.27)$$

for, $C_{P=0}$ and $C_{V=\alpha}$ are the heat capacities at zero pressures when the real gases behave as ideal ones.

Substituting the values of $\frac{dB}{dT}$ in equation (7.27),

(*i*) for van der Waals' gas

$$C_P - C_V = R + \frac{2a}{RT^2}P = R\left[1 + \frac{2aP}{R^2T^2}\right] \quad (\textit{cf. eqn } 7.25)$$

(*ii*) for Berthelot's gas,

$$C_P - C_V = R + \frac{27}{16}\,\frac{RT_c^3}{P_cT^3}P \qquad \ldots (7.28)$$

Example : Calculate the values of $(C_P - C_V)$ for a mole of oxygen at 27°C and 100 atmosphere pressure behaving as (*a*) van der Waals' gas, (*b*) Berthelot's gas. [a = 1.36 litre^2-atm, P_c = 35 atm, T_c = 135°K].

For the van der Waals' gas,

$$C_P - C_V = R\left(1 + \frac{2aP}{R^2T^2}\right) = 0.082\left(1 + \frac{2 \times 1.36 \times 100}{(0.082)^2(300)^2}\right) 24.2$$

$$= 2.986 \text{ calories}$$

For the Berthelot's gas,

$$C_P - C_V = R + \frac{27}{16}\,\frac{RT_c^3}{P_cT^3}P$$

$$= \left[0.082 + \left(\frac{27}{16}\cdot\frac{(0.082)\,(135)^3}{(35) \times (300)^3} \times 100\right)\right] \times 24.2 = 2.856 \text{ cal}$$

7.5. Joule-Thomson Effect

Joule's experiment, (Sec. 2.6) in free expansion of a gas into a vacuum revealed that the temperature-drop of the system was negligible and would be zero if the gas were ideal. But Joule and Thomson's subsequent experiments on the passage of a gas from a higher pressure to a lower one through fine orifices of a porous plug revealed a drop in temperature in many cases.

Suppose the volume V_1 of a gas under a constant pressure P_1

is allowed to pass through a porous barrier from the region on the left to the region on the right where the constant pressure is P_2. The volume of the gas becomes V_2. The process is carried out with the slow motion of the two frictionless pistons at the two ends (Fig. 7*a*). The whole system is thermally insulated, such that $q = 0$.

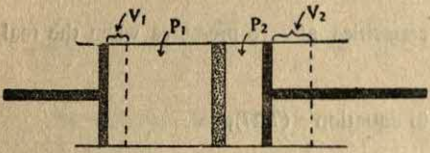

Fig. 7*a*

The work done by the piston on the left $= P_1V_1$

The work obtained from the system on the right $= P_2V_2$

Then, from the first law, $\triangle U = -W = P_1V_1 - P_2V_2$

or $U_2 - U_1 = P_1V_1 - P_2V_2$

or $U_1 + P_1V_1 = U_2 + P_2V_2$

or $H_1 = H_2$

or $\triangle H = 0$

This means that in the adiabatic expansion of a gas through fine orifices the heat-content remains unaltered. That is, such adiabatic expansion is also *isoenthalpic*. Nevertheless there is a drop of temperature *generally* of the outcoming gas and such variation of temperature is called *Joule-Thomson effect*.

The rate of change in temperature with pressure when enthalpy remains constant is called *Joule-Thomson coefficient*,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \qquad \ldots (7.29)$$

In such flow through fine orifices, usually the gas runs into lower pressures, *i.e.*, dP is negative. Hence μ will be positive if dT also is negative, *i.e.*, if temperature falls. At ordinary temperatures, most gases cool down in passing to lower pressures through porous plugs. Hydrogen and Helium, however, at room temperatures become heated instead of cooling, *i.e.*, μ is negative. We can explain this in the following way. We know,

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

In an isoenthalpic change like the above, $dH = 0$,

$$\therefore \quad \left(\frac{\partial H}{\partial T}\right)_P dT = -\left(\frac{\partial H}{\partial P}\right)_T dP$$

or $$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial H}{\partial P}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_P = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

o $$\mu = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T \qquad \ldots (7.30)$$

Since $H = U + PV$; $\mu = -\frac{1}{C_P}\left(\frac{\partial U}{\partial P}\right)_T - \frac{1}{C_P}\left(\frac{\partial (PV)}{\partial P}\right)_T$ ... (7.31)

In the case of an *ideal gas*, both the terms on the right-hand side separately vanish, for, $\left[\frac{\partial U}{\partial P}\right]_T = 0$, and $\left[\frac{\partial (PV)}{\partial P}\right]_T = 0$, hence $\mu = 0$.

The case of a real gas is different. Rewriting equation (7.31) as

$$\mu = -\frac{1}{C_P}\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{C_P}\left[\frac{\partial (PV)}{\partial P}\right]_T \qquad \ldots (7.32)$$

In this equation, $\left(\frac{\partial U}{\partial V}\right)_T$ of a gas is usually positive, while $\left(\frac{\partial V}{\partial P}\right)_T$ for any gas is always negative. As a result, the first term is always positive. The magnitude of the second term $\left[\frac{\partial (PV)}{\partial P}\right]_T$ may be negative or may be positive. At low temperatures and at low pressures, $\left[\frac{\partial (PV)}{\partial P}\right]_T$ is negative. Under such conditions both the terms in the equation being positive, μ has a positive value. That means that there would be a cooling of the gas. Even at ordinary temperatures, except for hydrogen and helium, all other gases show $\left[\frac{\partial (PV)}{\partial P}\right]_T$ negative at lower pressures. But at higher pressures $\left[\frac{\partial (PV)}{\partial P}\right]_T$ becomes positive so that second term becomes negative and if its value exceeds that of the first term, μ becomes negative. At high temperatures all gases have $\left[\frac{\partial (PV)}{\partial P}\right]_T$ positive, so μ is generally negative.

The cooling effect is observed at relatively low temperatures but if the temperature be high, then instead of cooling the gases become heated, *i.e.*, J-T effect μ becomes negative. For every gas there is a temperature where $\mu = 0$, when neither heating nor cooling of the gas due to passage through fine orifices would occur. This is called the '*inversion temperature T_i*' of the gas.

We shall now attempt to find a useful expression for μ. We have

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

(from Maxwell relations), $= \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$

Now $\quad dH = TdS + VdP$

Substituting dS in it, $\quad dH = T\left[\frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP\right] + VdP$

In an isoenthalpic change, $dH = 0$, hence

$$C_P dT = T\left(\frac{\partial V}{\partial T}\right)_P dP - VdP$$

$$= \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

or $\quad \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \quad \ldots (7.33)$

For a van der Waals gas,

$$PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$$

or $\quad V = \frac{RT}{P} - \frac{a}{PV} + b + \frac{ab}{PV^2} \approx \frac{RT}{P} - \frac{a}{RT} + b + \frac{abP}{R^2T^2} \quad \ldots (A)$

$$\therefore \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{a}{RT^2} - \frac{2abP}{R^2T^3} \quad \ldots (B)$$

But from (A), $\quad \frac{R}{P} = \frac{V-b}{T} + \frac{a}{RT^2} - \frac{abP}{R^2T^3} \quad \ldots (C)$

Substituting (*C*) in (*B*)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3}$$

$$\therefore \quad T\left(\frac{\partial V}{\partial T}\right)_P - V = (V-b) + \frac{2a}{RT} - \frac{3abP}{R^2T^2} - V$$

$$= \frac{2a}{RT} - b - \frac{3abP}{R^2T^2}$$

So, from eqn. (7.33) $\mu = \frac{1}{C_P}\left[\frac{2a}{RT} - b - \frac{3abP}{R^2T^2}\right]$ . . . (7.34)

At low pressure, the last term is negligible, and hence an *approximate* expression for *J-T* coefficient is

$$\mu = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right] \qquad \text{. . . (7.34}a\text{)}$$

The knowledge of heat-capacity and the van der Waals' constants would enable us to evaluate the Joule-Thomson effect at a given temperature *T*.

At high temperatures $\frac{2a}{RT} < b$, hence μ is negative. At low temperatures $\frac{2a}{RT} > b$, hence μ is positive. For hydrogen, where '*a*' is small, $\frac{2a}{RT}$ even for ordinary temperatures is less than '*b*', so there is heating in Joule-Thomson expansion. It must be remembered that in the adiabatic expansion of a gas, there is always a cooling effect due to the decrease in the int. energy in the performance of work. But in Joule-Thomson effect, cooling will occur only when μ is positive.

Putting $\mu = 0$, at the inversion temperature T_i,

$$\frac{2a}{RT_i} - b = 0,$$

or, $$T_i = \frac{2a}{Rb} \qquad \text{. . . (7.35)}$$

The inversion temperatures of some common gases are given here.

TABLE : INVERSION TEMPERATURES

Gas	He	H_2	A	N_2	CO_2	*air*
T_i(°K)	~40°	202°	723°	621°	~1500°	603°

A somewhat different attempt gives very interesting results. van-der Waals' equation, $PV + \frac{a}{V} - Pb - \frac{ab}{V^2} = RT$, on differentiation, gives

$$\left[P - \frac{a}{V^2} + \frac{2ab}{V^3}\right]\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\therefore\ T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{RT}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} - V$$

$$= \frac{-\,bP + \frac{2a}{V} - \frac{3ab}{V^2}}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

Hence from equation (7.33),

$$\mu = \frac{1}{C_P}\,\frac{-Pb + \frac{2a}{V} - \frac{3ab}{V^2}}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

At the inversion point, $\mu = 0$, hence

$$-\ Pb + \frac{2a}{V} - \frac{3ab}{V^2} = 0 \qquad \ldots (7.36)$$

$$\text{i.e.,}\qquad P = \frac{a}{b}\left[\frac{2}{V} - \frac{3b}{V^2}\right] \qquad \ldots (7.37)$$

or, from equation (7.36), multiplying by $-\frac{PV^2}{b}$, at the inversion point,

$$P^2V^2 - \frac{2a}{b}PV + 3aP = 0$$

$$\text{or}\qquad R^2T_i^2 - \frac{2a}{b}RT_i + 3aP = 0$$

$$\text{or}\qquad T^2 - \frac{2a}{Rb}T_i + \frac{3aP}{R^2} = 0 \qquad \ldots (7.38)$$

The equations (7.36, 7.37) satisfy the conditions at the inversion point. The consideration of these two equations leads to some important generalisations regarding the inversion temperatures.

(1) Firstly, equation (7.38) is a quadratic equation. Hence for a given value of P, there shall be two inversion temperatures. The plot of T_i against P would be parabolic as shown in Fig. 7*b*. This has been experimentally confirmed in the case of nitrogen by Roebuck and Osterburg (1935). For any point within the curve, μ would be positive ; outside the curve, value of μ would be negative.

(2) Secondly, from equation (7.37) for a given pressure P, there would be two different values of V. These, from the original equation of van der Waals, would give two inversion temperatures for a definite value of P.

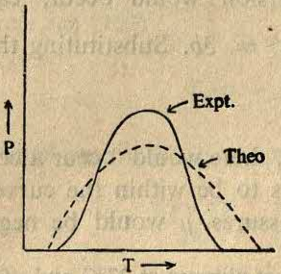

Fig. 7*b*
Inversion temperate curve

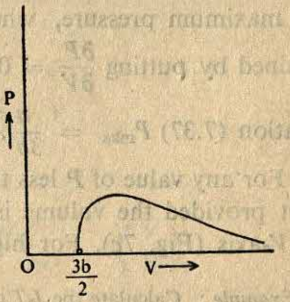

Fig. 7*c*
Inversion temperature of a gas

Now, the initial pressure P, may have any real value from zero to infinity. If equation (7.37) be plotted we obtain the graph as in Fig. 7*c*.

From the relation, $P = \frac{a}{b}\left[\frac{2}{V} - \frac{3b}{V^2}\right]$,

P would be positive only between the limits $V = \infty$ and $V = \frac{3b}{2}$.

Subtsituting this value of P in van der Waals' equation,

$$RT_i = \left[\frac{a}{b}\left(\frac{2}{V} - \frac{3b}{V^2}\right) + \frac{a}{V^2}\right](V-b) = \frac{2a}{b}\left[1 - \frac{b}{V}\right]^2 \quad \ldots(7.39)$$

The limiting values of T_i can be obtained by putting those of V in equation (7.39).

When $V = \infty$; $T_i = \dfrac{2a}{Rb}$ (*cf.* equation, 7.35) and

when $V = \dfrac{3b}{2}$; $T_i = \dfrac{2a}{9Rb}$

At $P = 0$, the T_i values have the limits $\dfrac{2a}{Rb}$ and $\dfrac{2a}{9Rb}$.

At other suitable pressures also there would be two inversion temperatures. At the lower inversion temperature, the Joule-Thomson effect changes from heating to cooling, while at the higher inversion temperature the effect changes from cooling to heating.

Equation (7.37) gives $$\frac{\partial P}{\partial V} = \frac{a}{b}\left[\frac{6b}{V^3} - \frac{2}{V^2}\right]$$

The maximum pressure, where inversion would occur, can be obtained by putting $\dfrac{\partial P}{\partial V} = 0$, *i.e.*, $V = 3b$. Substituting this in equation (7.37) $P_{\max} = \dfrac{a}{3b^2}$.

For any value of P less than this, there would occur a cooling effect provided the volume is such as to be within the curve and the V-axis (Fig. 7*c*). For higher pressures, μ would be negative.

Example : Calculate the *J-T* coefficient of nitrogen at 27°C and 100 atm as a van der Waals gas having a C_P-value 8.21 cal/mole-°K.

Given $a = 1.4$ litre²-atm/mole², $b = 0.04$ litre/mole.

Using eqn (7.34), we have

$$\mu = \frac{1}{C_P}\left[\frac{2a}{RT} - b - \frac{3abP}{R^2T^2}\right]$$

$$= \frac{1}{8.21 \times 0.0413}\left[\frac{2\times1.4}{0.082 \times 300} - 0.04 - \frac{3\times1.4\times0.04\times100}{(0.082)^2 \times 300^2}\right]$$

$$= 0.112\text{°K atm}^{-1}$$

If the approximate equation (7.34*a*) be used,

$$\mu \approx 0.21\text{°K atm}^{-1}$$

For liquefaction, it is essential that the gas should be cooled below its critical temperature. Even then high pressure and low temperature are required to liquefy most of the gases. Of course, the lower the temperature the lower would be the required pressure. In ordinary cases, refrigeration with ammonia or methyl-chloride or dry-ice-ether etc. is sufficient for liquefaction of many gases. But often very low temperatures are needed to liquefy common gases such as, O_2, N_2, He, H_2, etc. In such cases, Joule-Thomson cooling effect is taken advantage of.

The liquefaction of hydrogen and helium proved very difficult due to (*i*) their intermolecular forces being very small and (*ii*) their inversion temperatures and the critical temperatures being very low. Dewar (1898) succeeded in liquefying hydrogen for the first time by applying Linde's principle of regenerative cooling and using liquid air (evaporating under reduced pressure) as refrigerating agent, when a temperature of −200°C was reached. The gas was then made to suffer J-T expansion through a nozzle. After a few operations, the gas liquefied. Kammerling Onnes (1908) liquefied helium following a similar process and precooling the gas with liquid hydrogen. Helium has a cr. temperature of 5.25°K and indeed Onnes succeeded in reaching as low a temperature as 0.82°K. Kapitza (1934) liquefied both hydrogen and helium by using his 'expansion engine' with loose pistons without lubricants.

7-6. From a knowledge of C_P and μ it is possible to compute the molar volume at a desired temperature.

From eqn (7.33)

$$C_P\mu = T\left(\frac{\partial V}{\partial T}\right)_P - V$$

Multiplying with dT/T^2 we find

$$\frac{C_P\mu\, dT}{T^2} = \left[\frac{TdV - VdT}{T^2}\right]_P = d\left(\frac{V}{T}\right)_P$$

$$\text{Integrating}\quad \frac{V}{T} - \frac{V_0}{T_0} = \int_{T_0}^{T}\left(C_P\,\mu\frac{dT}{T^2}\right)_P$$

Hence V can be ascertained with reference to a standard for V_0 and T_0.

Problems

1. At 0°C and 1 atm, the data for lead given are

$C_P = 6.39$ cal/mole, $\quad v = 18.3$ cc/mole

$\alpha = 82\times10^{-6}$ deg^{-1}, $\quad \beta = 2.4\times10^{-12}$ cm^2/dyne

Find out C_V value for a mole of lead. **Ans.** $C_V = 6.06$ cal/mole

2. The molar heat-capacity of CO at 100°C and 1 atm is $C_P = 7.00$ cal/mole-degree. What will be its heat capacity at 50 atm at the same temperature? The gas behaves as a Berthelot gas, having $t_c = -140$°C, $P_c = 34.5$ atm.
Ans. 7.32 cal/mole-degree

3. For methane, the following data are given :

$$t_c = -82.5°\text{C}, \qquad P_c = 45.8 \text{ atm}$$

van-der Waals constants : $a = 3.59$ litre^2-atm/mole^2, $b = 0.0427$ litres/mole

Calculate $(C_P - C_V)$ for methane at a temp. of 100°C and 50 atm using (*i*) van-der Waals equation and (*ii*) Berthelot equation.

Ans. (*i*) 2.46 (*ii*) 2.47 cal/mole°K

4. The measured molar volumes of ammonia at different temperatures under a constant pressure of 40 atm are:

T(°K)	500	525	550	575	600
V(litres)	0.958	1.017	1.076	1.136	1.196

Calculate (*i*) The *J-T* coefficient at 300°C and 40 atm and (*ii*) the inversion temperature of ammonia, if $a = 4.0$ litre^2-atm-mole^{-2} and $b = 0.036$ litre-mole^{-1}.

What will be the *J-T* coefficient if calculated from van-der Waals equation?

Ans. (*i*) μ(graph) $= 0.34$, μ(van-dar Waals) $= 0.28$ (*ii*) $T_i = 2710°\text{K}$

5. Calculate *J-T* coefficient for oxygen at 0°C behaving as a van-der Waals gas. Given $C_P = 7.03$, $a = 1.36 \times 10^6$ cc^2-atm/mole^2 and $b = 32.0$ cc.

[C.U. 1963]

6. Compute C_V and β_S (adiabatic compressibility) for mercury at 0°C and 1 atm, if

$$C_P = 6.69 \text{ cal/mole}, \qquad \alpha = 181 \times 10^{-6} \text{ per degree}$$

$$\beta = 3.88 \times 10^{-12} \text{ cm}^2/\text{dyne} \qquad v = 14.7 \text{ cm}^3/\text{mole}$$

Ans. $C_V = 5.88$ cal/mole, $\beta_S = 3.4 \times 10^{-12}$ cm^2/dyne

7. The sp. volume of nitrogen at 20°C and 100 atmosphere was 8.64 cc/gm and $C_P = 8.21$ cal/mole. The coefficient of expansion, $\alpha = 0.0041$ deg^{-1}. Show that its Joule-Thomson coefficient $\mu = 0.142°$ atm^{-1}.

8. For a van der Waals gas, $a = 1.39$ lit^2-atm/mole^2 and $b = 3.92 \times 10^{-2}$ litres/mole. Calculate its $\mu_{J.T}$ at 20°C and 100 atmospheres if $C_P = 8.21$ cal/mole.

Ans. $\mu = 0.22°$ atm^{-1}

9. A gas follows the equation of state : $P(V-B) = RT$. Show that its *J-T* coefficient would be equal to $-B/C_P$.

10. Using van-der Waals equation estimate *J-T* coefficient for nitrogen at *S.T.P.* Given

$$t_c = -147°\text{C}, \quad P_c = 34 \text{ atm}, \quad C_P = 0.2466 \text{ cal/g°C}$$

11. Calculate specific heat of mercury at constant volume (C_V) at 0°C. Given

$$C_P = 0.0333 \; ; \; V\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1.0133 \times 10^6}{3.9 \times 10^{-6}} \text{ (atm), where}$$

$$V = \text{specific volume} = 1/13.596 \text{ cc.}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = 1.8 \times 10^{-5} V.$$

Ans. $C_V = 0.0292$

12. The inversion curve for Helium is represented by

$$P = 5.44T - 0.132T^2 - 21, \qquad (P \text{ in atmospheres})$$

Calculate the pressure at the maximum point of the inversion curve. What is the maximum inversion temperature?

Ans. (*i*) $P = 35$ atm, $T = 20.6°\text{K}$ (*ii*) $T \approx 37°\text{K}$

13. If the temperature-change with the change in pressure under isoentropic condition is given by $\mu_S = (\partial T/\partial P)_S$, show that $\mu_S - \mu = V/C_p$, where μ is the *J-T* coefficient.

14. Prove $$C_P.\mu = T^2 \left[\frac{\partial(V/T)}{\partial T}\right]_P$$

15. Establish $$\left(\frac{\partial P}{\partial T}\right)_S = \frac{\gamma}{\gamma-1}\left(\frac{\partial P}{\partial T}\right)_V$$

and $$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{1}{\gamma-1}\left(\frac{\partial V}{\partial T}\right)_P$$

[Hint : Begin with $\left(\frac{\partial P}{\partial T}\right)_S = -\left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial S}{\partial P}\right)_T$ and then transform]

16. Prove that $$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{\alpha VT}$$

CHAPTER 8

THE THIRD LAW OF THERMODYNAMICS

8.1. Nernst heat theorem

In 1902 Richards studied the thermodynamic changes in a number of galvanic cells at low temperatures and showed that with lowering of temperature $\triangle G$ and $\triangle H$ approach each other rapidly. That is, at extremely low temperatures. $\triangle G$ and $\triangle H$ tend to become equal. Hence,

$$Lt_{T\to o}\ \triangle G = \triangle H$$

Since,
$$\triangle G - \triangle H = T\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$$

then $$Lt_{T\to o}\ T\left[\frac{\partial(\triangle G)}{\partial T}\right]_P = 0$$

At $T = 0°\text{K}$, $T\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$ will be equal to zero, whether $\frac{\partial(\triangle G)}{\partial T}$ is a finite quantity or zero.

In 1906, Nernst made the bold postulate that for a process in a condensed system $\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$ will be zero in the vicinity of absolute zero. That is,

$$Lt_{T\to o}\left[\frac{\partial(\triangle G)}{\partial T}\right]_P = 0, \qquad \ldots (8.1)$$

i.e. at extremely low temperatures, $\triangle G$ would be constant.

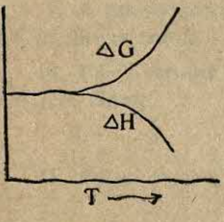

Fig. 8*a*

Nernst further suggested that not only $\triangle G$ and $\triangle H$ are equal at the absolute zero, but they approach equality in this temperature range asymptotically. The equality holds true for some range above and in the neighbourhood of absolute zero. Hence, the variation of $\triangle G$ and $\triangle H$ may be represented graphically as in Fig. 8*a*.

This then leads also to the conclusion that,

$$Lt_{T\to o}\ \frac{\partial(\triangle H)}{\partial T} = 0 \qquad \ldots (8.2)$$

Stated analytically then, the two postulates of Nernst for a condensed system, are

$$\left.\begin{aligned} Lt_{T\to 0}\,\frac{\partial(\triangle G)}{\partial T} &= 0 \\ Lt_{T\to 0}\,\frac{\partial(\triangle H)}{\partial T} &= 0 \end{aligned}\right\} \quad \ldots (8.3)^*$$

These constitute what we call the Nernst Heat Theorem. This innocent-looking pair of simple relations have however far-reaching consequences as we shall presently see.

Again, we know from definition, $\triangle G = VdP - SdT$

$$\text{or} \quad \left[\frac{\partial(\triangle G)}{\partial T}\right]_P = -\triangle S, \text{ (at constant pressure)} \quad \ldots (8.3a)$$

But in the vicinity of absolute zero, $\left[\frac{\partial(\triangle G)}{\partial T}\right]_P = 0$

$\therefore\ Lt_{T\to 0},\ \triangle S = 0\,;\ \ i.e.,\ S_2 = S_1$

In other words, the Heat-theorem may be stated as,

"*In the neighbourhood of absolute zero of temperature, the entropy-change associated with any isothermal reversible process tends to zero.*"

The Nernst's theorem refers only to the change in entropy but does not indicate the value of the entropy of the substance at 0°K.

Even then the theorem has some limitations.

(*i*) For example, if at 0°K, 1 mole of A and 1 mole of B be mixed or form a solution, then the entropy-change according to the theorem would be zero.

$$Lt_{T\to 0},\quad \triangle S = S_{AB} - S_A - S_B = 0$$

But for the mixing, the entropy-change is known to be positive,

$$Lt_{T\to 0},\ \triangle S = -R[\tfrac{1}{2}\ln\tfrac{1}{2} + \tfrac{1}{2}\ln\tfrac{1}{2}] = R\ln 2 = 1.4 \text{ cal/°K}$$

(*ii*) Again, suppose a substance is present in a crystalline form as well as in a supercooled liquid state at 0°K. The solidification of the supercooled liquid or vice-versa always would involve some entropy-change. The randomness in the supercooled liquid state is always greater than in the solid state. Hence $\triangle S \neq 0$. This obviously contradicts the theorem, according to which $Lt_{T\to 0}\ \triangle S = 0$.

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* Nernst in his orginal paper used the symbols A and U for free energy and the internal energy so that

$$Lt_{T\to 0}\frac{\partial A}{\partial T} = Lt_{T\to 0}\frac{\partial U}{\partial T} = 0$$

8.2. The Third Law

Inspite of its limitations, the Nernst Heat Theorem is the precursor of the more important fundamental principle enunciated by Planck, commonly called the *Third Law*. Since

$$Lt_{T\to 0}\left[\frac{\partial(\triangle H)}{\partial T}\right]_P = 0, \quad \text{and} \quad \left[\frac{\partial(\triangle H)}{\partial T}\right]_P = \triangle C_P,$$

hence one of the consequences of the Heat theorem is

$$Lt_{T\to 0}\ \triangle C_P = 0,$$

i.e. heat-capacities of the initial substances (or reactants) and the final substances (or resultants) at 0°K shall be the same.

From quantal principles, it was found that at very low temperatures, the heat-capacity C_P of a substance continuously diminishes with lowering of temperature and would ultimately vanish ;

i.e., $$Lt_{T\to 0},\ C_P = 0$$

This is also corroborated by experiments. Hence at low temperatures $\frac{C_P}{T}$ is zero or a finite quantity.

The entropy-change due to lowering of temperature is given by

$$\triangle S = \frac{q}{T} = \frac{C_P \triangle T}{T}$$

or $$\int_0^T dS = \int_0^T \frac{C_P dT}{T}$$

i.e., $$S_T - S_0 = \int_0^T \frac{C_P}{T} dT \qquad \ldots (8.4)$$

Since $\frac{C_P}{T}$ is a finite quantity, we can say $S_T - S_0$ must be a positive quantity *i.e.*, $S_T > S_0$. In other words, the entropy of a substance at any temperature must be greater than its entropy at absolute zero.

In 1906 Planck made the striking proposal in this regard and enunciated the third law as,

"*The entropy of a pure solid or a pure liquid is zero at the absolute zero of temperature.*'

For a condensed system,

(*i*) Nernst theorem states $Lt_{T\to 0},\ \triangle S = 0$

and (*ii*) Planck's Law states $Lt_{T\to 0},\ S = 0$

It is obvious that the third law does not contradict the Heat theorem rather it supports and makes the latter quantitative. At 0°K, the reactant solids have zero entropy as also the products have zero entropy, hence the entropy-changes, $\triangle S = 0$.

In the statement of the Third Law, emphasis has been laid on the *purity* of the substance, for, if the system at 0°K be a mixture or a solution, the entropy cannot be zero as has been shown in the previous section. According to Planck, the entropy of solutions at 0°K have a positive entropy which is equal to the entropy-change of mixing.

Even then the inclusion of *pure liquid* by Planck in the enunciation of the Third Law is not acceptable. A supercooled liquid at 0°K will have a greater randomness and hence a larger entropy than in its solid form. The supercooled liquids like glasses cannot have zero entropy but must possess a positive entropy. The Planck's principle would hence be true for *pure crystalline substances*. The third law has therefore been stated in the following form by Lewis and Randall (1923) :

"*Every system has a finite positive entropy but at the absolute zero of temperature the entropy may become zero and does so become in the case of a pure crystalline substance.*"

The third law is not a general one as the other laws of thermodynamics, for it applies only to pure crystalline substances and not to all kinds of substances.

Two relevant and important comments in respect of the third law should be mentined here.

I. Some solids such as sulphur, tin, phosphine, cyclohexanol etc. exist in two or more solid crystalline forms with definite transition points. The question is whether the different modifications will all have zero entropy at 0°K. The experiments have revealed that if the modifications exist in perfectly crystalline form, each one of them may be assigned zero entropy value at 0°K. The oft-quoted experiment on the measurement of entropy of β- and γ-forms of phosphine may be cited. At higher temperatures phosphine solid exists in α-form. At lower temperatures β- and γ-forms exist. The transition temp. (T_t) for $\beta \rightarrow \alpha$ is 49.43°K and for $\gamma \rightarrow \alpha$

is 30.29°K. The entropy of α-phosphine at 49.43°K was determined in two ways.

(*a*) The entropy of β-form from 0°K ~ 49.43°K was measured from heat-capacities and to this was added the entropy of transition $\beta \rightarrow \alpha$. The net-value of $S_\alpha = 8.14$ e.u. at 49.43°K.

(*b*) In the second experiment γ-phosphine was heated from 0°K ~ 30.29°K and entropy-rise was determined from heat-capacity measurements. At 30.29°, γ-form changed to α-form and entropy of transition was obtained. Next the α-form was heated from 30.29°K ~ 49.43°K and the entropy-rise was evaluated from C_P-values. The net-entropy value $S_\alpha = 8.13$ eu at 49.43°K This striking agreement in the results confirms that the two modifications have the same entropy at 0°K. The constant value of entropy at 0°K has been taken as zero, since exactly similar results are found with other varieties of enantiotropic substances both elements and compounds.

II. Investigations have revealed that some pure crystalline solids at 0°K do possess some entropy. For example, at 0°K the solid carbon monoxide has a molar entropy of 1 cal/°K and not zero. Similarly N_2O, NO-dimers (N_2O_2) etc. have residual entropies at 0°K. This is due to the randomised orientation of the molecules in the crystal lattice. The oxygen atoms of CO-molecules are in one direction in some points and oppositely directed at other points, as

CO OC CO OC
OC CO CO
CO OC CO CO etc.

If the randomisation were equal in two directions only, the entropy $S = k \ln W = k \ln 2^{N_o} = R \ln 2 = 1.4$ cal/°K. But the residual entropy is 1.0 cal/°K, which shows that it is not fully randomised.

Solid ice at 0°K has also a residual entropy. This is due to the randomness of the hydrogen bonding of water molecules in the crystal lattice.

At 0°K, solid hydrogen has a larger amount of entropy (about 1.5 e.u.). This is due to the fact that it is a mixture of ortho and para hydrogen and hence the entropy of mixing is involved. Further, pure para-hydrogen at 0°K has a zero entropy. But orthohydrogen can exist in any one of nine quantum states. This randomness also contributes a residual entropy to orthohydrogen.

It appears that for the application of the third law, the substance must be in *perfect* crystalline state and should be in a single quantum state.

8.3. Some Consequences of the Third Law

(*i*) By definition, $G = H - TS$ and $A = U - TS$

Hence at 0°K, when $S_0 = 0$,

$$G_0 = H_0 \quad \text{and} \quad A_0 = U_0$$

(*ii*) Since $S_0 = 0$, at 0°K

$$\therefore \quad \left(\frac{\partial S}{\partial P}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = 0$$

From Maxwell, $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$, and $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\therefore \text{ At } 0°\text{K}, \left(\frac{\partial V}{\partial T}\right)_P = 0, \text{ and } \left(\frac{\partial P}{\partial T}\right)_V = 0$$

That is, at the absolute zero of temperature the temperature coefficients of both pressure and volume are zero.

(*iii*) From equation (8.4), $S_T = \int_0^T \frac{C_p dT}{T} + S_0$

The third law states the entropy S must be finite at all temperatures. This means at 0°K, C_p must be zero. Otherwise at 0°K if C_p is finite, then S cannot be finite. Hence

$$Lt_{T \to 0}\, C_p = 0$$

Similarly, $$Lt_{T \to 0}\, C_v = 0$$

(*iv*) *Free energy change of a Process* : From equation (2.46*a*)

$$\triangle C_p = \alpha + \beta T + \gamma T^2 + \delta T^3 \ldots .$$

When $T = 0°\text{K}$, $\triangle C_p = C_{p_f} - C_{p_i} = \alpha + 0 + 0 + \ldots = 0$

Hence $\alpha = 0$; $\therefore \triangle C_{p_T} = \beta T + \gamma T^2 + \delta T^3 + \quad \ldots$ (8.5)

$$\text{Now } \triangle S = \int \frac{\triangle C_p dT}{T} = \int \frac{(\beta T + \gamma T^2 + \delta T^3 + \ldots)}{T} dT$$

$$= \beta T + \frac{\gamma}{2} T^2 + \frac{\delta}{3} T^3 + \ldots$$

Again from equation (2.47)

$$\triangle H_T = \triangle H_0 + \frac{\beta}{2} T^2 + \frac{\gamma}{3} T^3 + \frac{\delta}{4} T^4 + \ldots \quad \ldots (8.6)$$

$$\therefore \quad \triangle G_T = \triangle H_T - T\triangle S$$

$$= \left[\triangle H_0 + \frac{\beta}{2}T^2 + \frac{\gamma}{3}T^3 + \frac{\delta}{4}T^4 + \dots\right]$$

$$- \left[\beta T^2 + \frac{\gamma}{2}T^3 + \frac{\delta}{3}T^4 + \dots\right]$$

$$= \triangle H_0 - \frac{\beta}{2}T^2 - \frac{\gamma}{6}T^3 - \frac{\delta}{12}T^4 - \dots \qquad \dots (8.7)$$

It is thus possible to estimate the free energy change ($\triangle G$) at a given temperature for even a process involving solids from thermal data. An application of this is cited here.

Example : *Transition point of sulphur* : In the transformation of α- and β-sulphur, we may write, from equation (8.5)

$$\triangle C_P = \beta T$$

Measuring the heat-capacities of the two forms at a known temperature, the value of β was found to be 2.30×10^{-5}. The heat of transformation $\triangle H_T$ at a temperature T was also measured, from which $\triangle H_0$ was calculated as 1.57; for

$$\triangle H_0 = \triangle H_T - \frac{\beta}{2}T^2 = 1.57 \quad \text{(eqn 8.6)}$$

At the transition temperature T_ϵ, the two modifications of sulphur are in equilibrium, *i.e.*, $\triangle G_\epsilon = 0$.

$$\triangle G_\epsilon = \triangle H_0 - \frac{\beta}{2}T^2_\epsilon = 1.57 - 1.15\times10^{-5}T^2_\epsilon = 0$$

or $\quad T_\epsilon = 369.5$°K ; [Expt. value $T_\epsilon = 368.4$°K]

The fusion temperature of solids may also be similarly calculated.

(*v*) We know, from equation (5.25),

$$S = k \ln W$$

where W is the thermodynamic probability. At 0°K, the third law states, $S_0 = 0$. In other words,

$$\ln W = 0, \qquad \text{or} \qquad W = 1$$

The system must be in a perfect order without any multiplicity of microstates at absolute zero of temperature.

Some qualitative generalisations can be made with regard to entropies of substances and their properties.

Generally the molar entropies increase with the complexity of the molecules. This is illustrated in the table below :

Substance	*molar e.u.*	*Substance*	*molar e.u.*
NaCl	17.3	$CuSO_4$	27.1
$PbCl_2$	32.6	$CuSO_4, 5H_2O$	73.0
$AlCl_3$	40.0		
$SnCl_4$	62.5		
PbO	16.6	CH_4	44.5
Pb_2O_3	18.3	C_2H_6	54.8
Pb_3O_4	50.5	C_3H_8	64.7

Due to perfect order pure crystalline substances have zero entropy at 0°K. Rigid crystalline substances having directional bonds have very small entropies owing to perfectly ordered arrangements within. Thus, diamond has an entropy 0.585, boron 1.7, silicon 4.5, e.u. Harder metals have smaller entropies. Fe 6.5, Ni 7.12, Be 2.28 e.u., etc. But softer metals having non-directional bonds have relatively higher molar entropies, e.g., Cd 12.3, Pb 15.5, K 15.2, e.u. etc. at 25°C.

The entropy-change per mole in vaporisation for normal liquids is practically the same, 21 e.u. (see Sec 13-3). The entropy increase in melting is only about 3 e.u. per mole. This is because disorderliness is much greater in vaporisation than in fusion.

Entropy also influences our existence in various ways. Some instances are mentioned. (*i*) Our ever-increasing demand of power is met from burning of coal or oil or from nuclear reactors. To produce work, in both cases, considerable waste heat is given up to the surroundings or atmosphere which serves as sink. This not only increases entropy but also increases *thermal pollution.* (*ii*) The food we take are mostly made up of very complex molecules which break up into a large number of simpler waste products during assimilation. This leads to increase in entropy. This can be minimised by taking food in much simpler form of molecules, instead of rearing animals for food consumption.

8.4. The Principle of unattainability of Absolute Zero

The Third Law has also been stated in an elegant fashion as: *It is impossible to attain absolute zero in a finite number of operations.*

That is, we cannot by any process occuring in finite dimensions cool a body to absolute zero of temperature.

I. It may be understood by considering a reversible cyclic process with a condensed system as represented in fig 8*b*. Let the condensed system be represented by the point P at temperature T, which is somewhat higher than absolute zero (T'). The system is allowed to undergo an isothermal expansion along *pq* to the point *q* by reversibly absorbing heat Q_1. The entropy of the system at *p* and *q* would be different.

It is then insulated and subjected to an adiabatic expansion represented by *qr*, until the temperature drops to absolute zero (T').

In the next step, the system undergoes isothermal expansion at T' (= 0°K) to the point *s* along *rs*. Finally, by adiabatic compression along *sp*, the system is returned to the orignial state *p*. The net work would be the area *pqrs*.

The following facts now deserve consideration.

(*i*) Let the entropies of the system along adiabatic *qr* and *ps* be s_1 and s_2. It is well-known that two adiabatics cannot intersect. [For, suppose in the inset (*L*), two adiabatics *xy* and *zy* having entropies s' and s'' intersect at *y*, then the system may be made to pass reversibly from *x* to *z* by a completely adiabatic path *xyz* and yet with a change in entropy form s' to s'', which is absurd.]

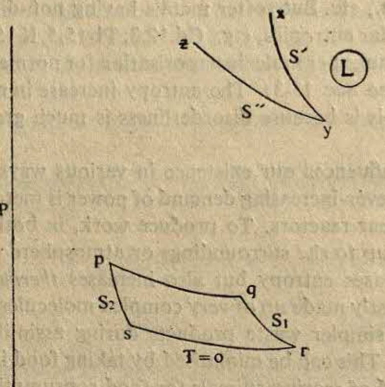

Fig. 8*b*

(*ii*) Now let us focus our attention to the process represented by *rs*, this is an isothermal process and as such during the shift from *r* to *s*, the entropy may change by $\triangle S$ ($= S_2 - S_1$). But along this path, the temperature is zero ($T = 0$), and the heat transferred is given by

$$\delta q = T.\triangle S = 0 \times \triangle S = 0$$

i.e., no heat change would occur. Since C_P is zero at $(T = 0)$, heat-exchange with the reservoir is nil, this isothermal has thus the peculiarity of undergiong no heat-exchange with the surrounding reservoir. That is the path *rs* is also an adiabatic. So the adabatic path *rs* cuts two other adiabatics, which is not permissible.

Again at the points *r* and *s*, *T* is zero, hence according to the third law, $S = 0$ at both these points. Since entropy remains constant along adiabatics, the entropies at *p* and *q* should also be zero, which is not true.

In other words, the imaginary cyclic process cannot be realised and cannot exist with the lower temperature process at the absolute zero. In consequence of the fact that $S = 0$, when $T = 0$, the absolute zero of temperature cannot be attained in practice. This is why the statement mentioned above is considered as the third law.

II. It may also be arrived at in other ways. Suppose a body at a low temperature (T'°K) is being cooled further by withdrawing heat from it with the help of a reversible refrigeration engine working between T°K and T'°K, $(T>T')$, minimum work (w) needed to extract Q heat from the cold body would be

$$w = \frac{T-T'}{T'}Q, \qquad \text{(eqn 4.17)}$$

Now as the temperature T' is lowered, more ana more work would be needed to extract the same ammount of heat. If the temperature of the body is lowered to 0°K, (*i.e.*, $T' = 0$°K), then infinite amount of work would be required. That is, any finite amount of work would not be sufficient to cool the body to 0°K. Hence, absolute zero of temperature cannot be attained.

III. The same can be formally derived as follows. Suppose a substance A at T_2°K be cooled to a substance B at T_1°K ; *i.e.*, $T_2>T_1$. A and B may be perfect crystals of two enantiotropic forms; or A may be a magnetised salt while B is the demagnetised form.

Their entropies would be

$$S_{A(T_2)} = S_{A(o)} + \int_0^{T_2} \frac{C_A dT}{T}$$

$$S_{B(T_1)} = S_{B(o)} + \int_0^{T_1} \frac{C_B dT}{T}$$

Now $Lt_{T\to 0}$ $S_{A(o)} = S_{B(o)}$; and for the cooling process to occur, entropy-change must be greater or equal to zero.

$$\int_0^{T_1} \frac{C_B dT}{T} \geqslant \int_0^{T_2} \frac{C_A dT}{T}$$

C_A, C_B are positive quantities. The starting temp. T_2 is greater than zero and hence positive. Hence the rt-hand integral is positive. This makes left-hand integral also positive,

$$\text{or} \qquad \int_0^{T_1} \frac{C_P dT}{T} > 0$$

This cannot be positive unless $T_1 > 0$. That is, the lowest temperature T_1 will always be positive. The absolute zero of temperature cannot be reached.

The three laws of thermodynamics may now be considered as admission of our failures gathered from experience,

First Law : *It is impossible to construct a device which continuously produces energy out of nothing.*

Second Law : *It is impossible to construct a device which will continuously transform heat into work completely.*

Third law : *It is impossible to device in practice an arrangement to cool a body to the absolute zero by completely depriving it of its heat.*

8.5. Determination of entropy

The most important application of the third law is in the measurement of the entropy of a substance.

We have from eqn (8.4),

$$S_T - S_0 = \int_0^T \frac{C_P}{T} dT$$

From the third law, for a pure crystalline substance, $S_0 = 0$. Hence,

$$S_T = \int_0^T \frac{C_P}{T} dT = \int_0^T C_P d\ln T = 2.303 \int_0^T C_P d\log T$$

This shows that if C_P be plotted against log T as in Fig. 8c(I) or alternatively, $\frac{C_P}{T}$ plotted against T as in Fig. 8c(II) the entropy

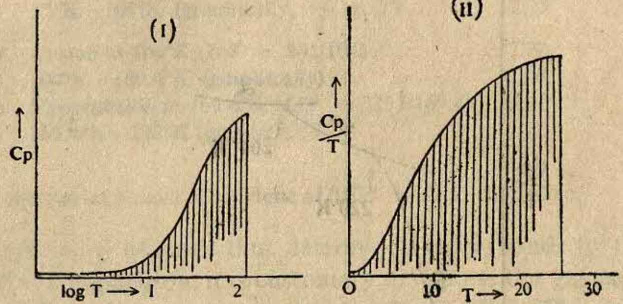

Fig 8c. The graphical determination of entropy

S_T can be graphically computed from the shaded areas of the figures. Obviously it requires the knowledge of the heat capacities C_p from the temperature T to the absolute zero. In practice however C_P cannot be measured at absolute zero or near about it. The measurements of the heat-capacities are carried out to as low a temperature as that of liquid hydrogen. Below liquid hydrogen temperature, extrapolation is permissible with the aid of the Debye equation,

$$C_V = 464.5\ T^3/\theta^3$$

where θ is a constant for the substance. From a determination of C_v at an appreciably higher temperature T, the magnitude of θ is known. Substituting θ in the equation above, the values of C_v in the vicinity of absolute zero are calculated. At extremely low temperatures the differences of C_P and C_v are negligible, so that these values may be used for C_P in the extrapolation of the curves (Fig. 8c).

Example : In the case of rhombic sulphur, the C_P values were calculated by Debye equation and $\frac{C_P}{T}$ vs. T was plotted.

The value of the entropy from 0°K to 30°K (Debye) = 0.12 cal/degree-mol.

The value of the entropy from 30°K to 298°K = 7.50 cal/degree-mol.

Hence, the net entropy of the rhombic sulphur per mole, (measured graphically), S = 7.62 cal/degree.

This method is also extended to determine the entropy of gases or liquids, in which the entropy-rise in the fusion or vaporisation of the substance is also to be added. In cases where the transition of solids occurs, the entropy-change due to transition must also be considered. Two examples are given here.

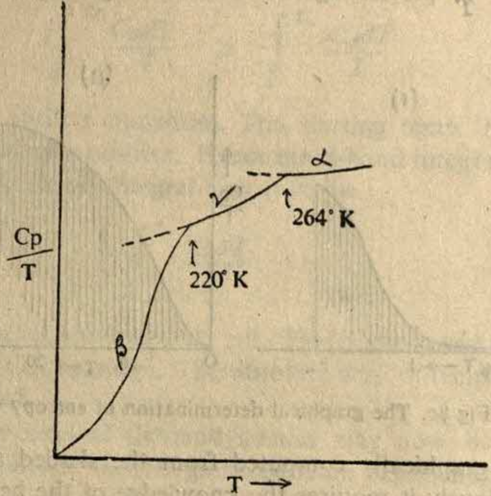

Fig 8*d*. The entropy of a mole of CH_3NH_3Cl at 25°C

Example 1. *The entropy of methyl ammonium chloride (solid) at* 25°C. (Aston et al, 1946).

The C_p-values were determined down to 12°K and in the region between 0°K and 12°K the values were calculated (Debye). Between 0°K and 298°K (25°C), there exist three different forms of solid, $\beta \rightarrow \gamma \rightarrow \alpha$ forms. The entropy-changes at the two transition temperatures at 220°K and 264°K were also considered from the heats of transition (Fig. 8*d*).

	ΔS	
0°K−12°K (extrapolation)	0.067	
12°K−220°K (β-form, graphically)	22.326	
Transition ($\beta \rightarrow \gamma$) at 220°K	1.929	(L_t = 425.2)
220°K−264°K (γ-form, graphically)	3.690	
Transition ($\gamma \rightarrow \alpha$) at 264°K	2.547	(L_t = 673.6)
264°K−298°K (α-form, graphically)	2.555	
	33.114	

∴ Entropy of one mole of solid CH_3NH_3Cl at 298°K is33.114 cal/degree.

Example 2. The entropy of ethylene gas at 25°C.

		$\triangle S$
(*i*)	0°K–15°K (by extrapolation with Debye)	0.24
(*ii*)	15°K–104°K (graphically, $\frac{C_P}{T}$ *vs. T*)	12.25
(*iii*)	Fusion at 104°K (L/T = 801/104)	7.70
(*iv*)	104°K–169.4°K (graphically)	7.90
(*v*)	Vaporisation at 169.4°K (L/T = 3237/169.4)	19.10
(*vi*)	169.4°K–298°K (graphically)	5.12
		52.31

The entropy of a mole of ethylene at 25°C = 52.31 cal/degree.

The entropy of gases thus determined corresponds to the real gases. For comparision, it is customary to express the gas-entropies in terms of ideal gases at one atm usually at 25°C. This is called the *standard entropy* or *the absolute entropy* of a gas. It is, hence, necessary to introduce correction terms to the observed entropy. This correction term may be obtained in the following way :

Let S_1 = entropy of the real gas (observed) at 1 atm.

and S_P = entropy of the real gas at p atm, where $Lt_{P\to 0}$

From Maxwell's relation,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

or

$$\triangle S_T = -\int\left(\frac{\partial V}{\partial T}\right)_P dP$$

or

$$S_1 - S_P = -\int_P^1\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \ldots (i)$$

Again, if we take an ideal gas, instead of a real one, and represent the entropies by S° symbols, then

$$S_1^\circ - S_P^\circ = -\int_P^1\left(\frac{\partial V}{\partial T}\right)_P dP = -\int_P^1\frac{R}{P}\,dP \qquad \ldots (ii)$$

Since at very low pressure P, real gases behave like ideal ones, we have $S_P = S_P^\circ$. Then subtracting (*i*) from (*ii*),

$$S_1^\circ - S_1 = \int_P^1\left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{R}{P}\right] dP$$

For a real gas, obeying Berthelot's relation,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{27}{32}\cdot\frac{RT_c^3}{P_cT^3} \quad \text{[see Sec. (7.3) example]}$$

$$\therefore \quad S_1^\circ - S_1 = \int_P^1 \frac{27}{32} \frac{RT_c^3}{P_cT^3} dP \approx \frac{27}{32} \frac{RT_c^3}{P_cT^3}, \quad (Lt_{P \to 0})$$

$$\approx \frac{27}{32} \cdot \frac{RT_c^3}{P_cT^3} \text{ (when } P \text{ is infinitely small.)}$$

This is therefore the difference between the ideal entropy and the observed entropy. In other words, the observed entropy should be corrected by $\frac{27}{32} \cdot \frac{RT_c^3}{P_cT^3}$ units.

In the example of ethylene cited above, the observed entropy is 52.31, e.u. The correction for imperfection should be

$$\frac{27}{32} \frac{RT_c^3}{P_cT^3} = \frac{27}{32} \cdot \frac{2 \times (282)^3}{50.7 \times (298)^3} = 0.028 \text{ e.u.}$$

$[P_c = 50.7 \text{ atm}, T_c = 282°\text{K}, \text{ for ethylene}]$

The absolute entropies of certain substances at 1 atm and 25°C calculated from the thermal data are given below:

TABLE : THE ENTROPIES AT 298°K

Substance		*Entropy*	*Substance*		*Entropy*
H_2 (*g*)	...	31.21	H_2O (*l*)	...	16.72
O_2 (*g*)	...	49.00	HCl (*g*)	...	44.62
N_2 (*g*)	...	45.77	HBr (*g*)	...	47.44
Cl_2 (*g*)	...	53.31	HI (*g*)	...	49.31
Br_2 (*l*)	...	36.40	CO (*g*)	...	47.30
I_2 (*s*)	...	27.90	CO_2 (*g*)	...	51.06
C (graphite)	...	1.36	NH_3 (*g*)	...	46.80
Ag (*s*)	...	10.21	NO (*g*)	...	50.34
Na (*s*)	...	12.20	NaCl (*s*)	...	17.30
S (rhombic)	...	7.60	KCl (*s*)	...	19.90
Fe (*s*)	...	6.71	CuO (*s*)	...	10.40
Zn (*s*)	...	9.83	BaO (*s*)	...	16.80
Hg (*l*)	...	17.80	$Ca(OH)_2$ (*s*)	...	17.40
Al (*s*)	...	6.75	AgCl (*s*)	...	23.00
$BaCO_3$	...	26.8	FeO	...	13.4
$PbCO_3$	...	48.5	Fe_2O_3	...	21.5
$ZnSO_4$	...	30.7	Al_2O_3	...	12.5
$BaSO_4$	...	31.5	MgO	...	6.55
CH_4 (*g*)	...	44.50	CH_3OH (*l*)	...	31.00
C_2H_4 (*g*)	...	52.45	C_2H_5OH (*l*)	...	38.40
C_2H_2 (*g*)	...	48.00	CH_3COCH_3 (*l*)	...	47.80
C_6H_6 (*g*)	...	64.34	CH_3COOH (*l*)	...	38.20
$C_6H_5CH_3$ (*g*)	...	76.42	$C_2H_5OC_2H_5$ (*l*)	...	60.40

The application of the third law in the determination of equilibrium constants in chemical processes will be discussed later.

The entropy-change in a chemical process can be computed from the individual entropies of the participants. Moreover, if heat of reaction ($\triangle H^\circ$) be known, the Gibbs' potential-change $\triangle G$ can also be evaluated.

Example : In the reaction,

$$NO\ (g) + CO\ (g) = \tfrac{1}{2}N_2\ (g) + CO_2\ (g)$$

Calculate $\triangle S^\circ$ and also $\triangle G^\circ$, of the process.

$$\begin{aligned}\triangle S^\circ &= \tfrac{1}{2}S^\circ(N_2) + S^\circ(CO_2) - S^\circ\ (NO) - S^\circ(CO)\\ &= 22.8 + 51.1 - 50.3 - 47.3 = -23.7\ \text{cal/degree.}\end{aligned}$$

Again, using standard tables for $\triangle H^\circ$, heats of formation,

$$\begin{aligned}\triangle H^\circ &= \tfrac{1}{2}\triangle H^\circ(N_2) + \triangle H^\circ(CO_2) - \triangle H^\circ(NO) - \triangle H^\circ\ (CO)\\ &= \tfrac{1}{2}\times 0 + (-94.0) - (21.6) - (-26.4) = -89.3\ \text{Kcal}\\ \therefore\ \triangle G^\circ &= \triangle H^\circ - T\triangle S^\circ = -89300 - 298\ (-23.7) = -82237\ \text{cal}\end{aligned}$$

The reaction is thermodynamically feasible at 25°C.

8.6. Tests of the third law

Several experimental facts can be cited to establish the truth of the third law.

(*a*) It is a prediction of the law that in the neighbourhood of the absolute zero, the heat-capacity and of coefficient of expansion would vanish. These have been confirmed experimentally in many instances.

(*b*) It is possible to calculate the change in entropy in the transition of one form of a substance into another form. The calculated values correspond to the experimental result.

Suppose there are two crystalline forms X and Y of an element. At the transition temperature T_t, $\triangle G = 0$. Hence, the entropy change,

$$S_Y - S_X = \frac{\triangle H}{T} \qquad \dots (a)$$

By the third Law, for both X and Y, the entropy value at $T = 0$ is zero, *i.e.*, $S_X = S_Y = 0$ ($Lt.\ T \rightarrow 0$). Then at temperature T_t,

$$S_X = \int_0^{T_t} \frac{C_X}{T}\,dT \qquad \text{and} \qquad S_Y = \int_0^{T_t} \frac{C_Y}{T}\,dT$$

$$\text{or} \qquad S_Y - S_X = \int_0^{T_t} \frac{C_Y - C_X}{T}\, dT \qquad \ldots (b)$$

The two methods (*a*) and (*b*) give the same value of the entropy-change. This has been studied in the case of white tin - grey tin, quartz-cristobalite, calcite-aragonite etc. The most satisfactory results were obtained with tin, which confirms the third law.

Brönsted studied the thermal properties of the two forms of tin. He found that S_{298} (white) = 11.17 and S_{298} (grey) = 9.23, so that $\triangle S_{298} = -1.94$. From the measured heat of transition and free energy, the value of $\triangle S_{298} = -1.87$, which is quite satisfactory.

(*c*) On the other hand, if we have a cell with grey tin as one electrode and white-tin as the other electrode dipped in a suitable electrolyte and if we measure the temperature coefficient of the cell, then $\triangle S$ would be known. For, by Gibbs Helmholtz relation,

$$\triangle S = \frac{\triangle H - \triangle G}{T} = n\mathscr{F}\frac{\partial E}{\partial T}$$

The value thus obtained agrees with the value obtained from heat-capacity data with the third law.

Similarly, in the following reactions, $\triangle G$ and $\triangle H$ were separately determined (from *e.m.f.*) and calorimetric measurements and $\triangle S$ is calculated. These values compared favourably with those obtained from the third law.

TABLE : ENTROPY-CHANGES

Chemical Process	$\triangle S$ (Gibbs-Helmholtz)	$\triangle S$ (third law)
Sn (white) → Sn (grey)	−1.87	−1.94
$Ag + HgCl = AgCl + Hg$	+7.78	+7.70
$\frac{1}{2}Pb + AgI = Ag + \frac{1}{2}PbI_2$	−3.99	−3.69

(*d*) The entropy-change, say at room temperature, of the reaction

$$2Ag + Cl_2 = 2AgCl$$

is given by $\qquad \triangle S = 2S_{AgCl} - 2S_{Ag} - S_{Cl_2}$

or $\qquad S_{Cl_2} = 2S_{AgCl} - 2S_{Ag} - \triangle S$

The value of $\triangle S$ can be determined experimentally from a knowledge of $\triangle G$ and $\triangle H$ of the process. Moreover, S_{AgCl} and S_{Ag} are ascertained from the heat-capacity data with the third law. Thus we know the entropy of chlorine, S_{Cl_2}. The value thus obtained approaches the value of S_{Cl_2}, directly determined by the third law. This indeed is a proof of the validity of the law.

(*e*) From considerations of statistical mechanics, the entropy of a monatomic substance (mol. wt. *M*) at a temperature *T* and pressure *P* has been shown to be

$$S = R \ln \left[\frac{(2\pi MkT)^{3/2}}{Nh^3} \cdot \frac{RT}{P} + \frac{5}{2} \right]$$

In case of polyatomic molecules, vibrational and rotational contributions are also to be considered.

Now, the entropies calculated with the help of the statistical formulae are found to be almost the same as determined from the third law. Some of the results are given below:

TABLE : ENTROPIES

Substance	S (Third Law)	S (Statistical)
Helium	29.2	29.8
Argon	36.4	37.0
Mercury Vapour	41.3	41.5
Hydrogen Chloride	44.5	44.6
Cadmium	40.0	39.8

Problems

1. Show that $\triangle S^\circ_T = \triangle S^\circ_{T_0} + \int_{T_0}^{T} C_P d \ln T$

In the reaction, $Cu_2O + C = 2Cu + CO\ (g)$, $\triangle H^\circ = +3000$ cal. The standard entropy of $Cu_2O = 24.1$ e.u. Evaluate the lowest temperature at which the reaction is thermodynamically feasible. Compute the value of $\triangle G$ at 127°C. [use table of entropies]

2. In a voltaic cell, $\overset{-}{Zn}-ZnSO_4, 7H_2O \parallel Hg_2SO_4-\overset{+}{Hg}$, the net heat-change for the chemical reaction involved is $\triangle H = -33360$ cal/gm-equivalent. The difference in heat capacities of reactants and resultants $\triangle C_p = 0.95$ cal. Use Nernst Heat theorem to compute the e.m.f. of the cell. [Hints. Evaluate $\triangle H^\circ$ with β derived from $\triangle C_p$ and then find $\triangle G$]. **Ans.** $E = 1.459$ volts

3. For Nitrogen, the following experimental data are given :

Debye function, $\theta = 68$; Transition temp. of solid nitrogen 35.0°K ($\triangle H_t = 54.7$ cal), m.pt. 63.2°K ($\triangle H_f = 172.3$ cal), b. pt. 77°K ($\triangle H_{vap} = 1333$ cal).

$$\int_{10°K}^{35} dS = 6.04 \text{ e.u.}; \quad \int_{35°K}^{63.2} dS = 560 \text{ e.u.}; \quad \int_{63.2°K}^{77} dS = 2.73.$$

Show that the entropy of nitrogen at its boiling point is about 36 e.u. per mole.

4. For chlorine, $\int_{0°K}^{171.1} dS = 16.9$ e.u.; m. pt. 171°K ; b. pt. = 239°K ;

$$\int_{171.1}^{239} dS = 5.23 \text{ e.u.} ; \ C_p = 8.2 \text{ cal}, L_f = 1522.8 \text{ cal}, L_{vap} = 4875.6 \text{ cal}.$$

Calculate entropy of chlorine at 25°C and 1 atm. pressure.

Ans. $S^\circ_{298} = 53.4$ e.u.

5. Calculate the entropy of a gm-atom of silver form a suitable graph with following data:

Temp°K	15	30	50	100	150	200	250	300
Cp (cal)	0.16	1.14	2.78	4.79	5.49	5.80	5.91	6.09

At $T = 0°K$, $C_p = 0$, and assume $C_p = \text{const}\ T^3$ is valid in the vicinity of absolute zero.

CHAPTER 9

PARTIAL MOLAL QUANTITIES : CHEMICAL POTENTIAL

9.1. Partial Molal Quantities

For *closed* systems, in which mass and chemical composition are fixed, the thermodynamic properties (such as, free energy, entropy, enthalpy etc.) depend usually on three parameters, P, V, T of the system. These are interrelated through some equation of state, so that any two of them can be taken as independent variables. So, any thermodynamic property, X, may be expressed as,

$$X = f(P, T) \; ; \quad X = f'(P, V), \text{ etc.}$$

In *open* systems in which mass and chemical composition may change, the extensive properties like, U, F, S, V, etc. must depend upon the amounts of the components present in the system. So, any extensive thermodynamic property, X, should be represented as,

$$X = f(P, T, n_1, n_2, n_3, \ldots)$$

where n_1, n_2, n_3 . . . etc. are the quantities of 1st, 2nd, 3rd components in the system usually expressed in gm-moles.

Let us now consider small changes in all the variables of the system, including the amounts of the components. The net change in the thermodynamic property, X, will be given by,

$$dX = \left(\frac{\partial X}{\partial P}\right)_{T,n_1,n_2,\ldots} dP + \left(\frac{\partial X}{\partial T}\right)_{P,n_1,n_2,\ldots} dT + \left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,n_3,\ldots} dn_1 + \\ + \left(\frac{\partial X}{\partial n_2}\right)_{P,T,n_1,n_3\ldots} dn_2 + \left(\frac{\partial X}{\partial n_3}\right)_{P,T,n_1,n_2\ldots} dn_3 + \ldots$$

The term $\left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,n_3,\ldots}$ is called the *partial molal property for* the first component and obviously denotes the rate of change of X on addition of one mole of the first component when all the other variables remain unchanged. This is usually denoted by putting a bar over the symbol for the property, such as $\bar{X}_1$. The partial molal properties of the different components, then, would be,

$$\bar{X}_1 = \left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,n_3\ldots} \; ; \quad \bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_1 n_2\ldots} \; ;$$

If the system undergoes a change only in the masses of its components, at *constant pressure and temperature*, we have,

$$dX_{P,T,} = \left(\frac{\partial X}{\partial n_1}\right)_{P,T,n_2,n_3\ldots} dn_1 + \left(\frac{\partial X}{\partial n_2}\right)_{P,T,n_1,n_3\ldots} dn_2 + \left(\frac{\partial X}{\partial n_3}\right)_{P,T,n_1,n_2\ldots} dn_3 + \ldots$$

$$= \bar{X}_1 dn_1 + \bar{X}_2 dn_2 + \bar{X}_3 dn_3 + \ldots \qquad \ldots (9.1)$$

It may be remembered that X stands for any extensive thermodynamic property. Thus, at constant temperature and pressure, we may express the changes of the volume or entropy as follows :

$$dV_{P,T,} = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2,n_3\ldots} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{P,T,n_1,n_3\ldots} dn_2 + \left(\frac{\partial V}{\partial n_3}\right)_{P,T,n_1,n_2} dn_3 + \ldots$$

$$= \bar{V}_1 dn_1 + \bar{V}_2 dn_2 + \bar{V}_3 dn_3 + \ldots$$

Or,

$$dS_{P,T} = \left(\frac{\partial S}{\partial n_1}\right)_{P,T,n_2,n_3\ldots} dn_1 + \left(\frac{\partial S}{\partial n_2}\right)_{P,T,n_1,n_3\ldots} dn_2 + \left(\frac{\partial S}{\partial n_3}\right)_{P,T,n_1,n_2\ldots} dn_3 + \ldots$$

$$= \bar{S}_1 dn_1 + \bar{S}_2 dn_2 + \bar{S}_3 dn_3 + \ldots$$

That is,

Partial molal volume of the 1st component $= \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2,n_3\ldots} = \bar{V}_1$

Partial molal entropy of the 2nd component $= \left(\frac{\partial S}{\partial n_2}\right)_{P,T,n_1,n_3} = \bar{S}_2$

Similarly, for the ith component in a system

Partial molal internal energy $= \left(\frac{\partial U}{\partial n_i}\right)_{P,T,n_1,n_2\ldots} = \bar{U}_i$

Partial molal enthalpy $= \left(\frac{\partial H}{\partial n_i}\right)_{P,T,n_1,n_2\ldots} = \bar{H}_i$

etc, etc, etc.

9.2. Chemical potential

The change in the free energy, G, may also be expressed, *at a constant temperature and pressure*, in the same way :

$$(dG)_{P,T} = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2,n_3\ldots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1,n_3\ldots} dn_2 + \ldots$$

$$= \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 + \ldots \qquad \ldots (9.2)$$

The partial molal free energy denoted by $\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_1,n_2\ldots}$ for the ith component has been given the name *chemical potential* by Willard Gibbs universally represented by the symbol μ_i .

$$i.e., \qquad \left(\frac{dG}{dn_i}\right)_{P,T,n_1,n_2\ldots} = \bar{G}_i = \mu_i$$

$$\therefore \quad dG_{P,T} = \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots \qquad \ldots (9.3)$$

The chemical potential μ_i therefore is a measure of the free energy of Gibbs potential increase of the system due to addition of 1 mole of the ith component at *constant temperature and pressure* when other components remain unaltered. This, it would be soon realised, has a unique importance in dealing with the various processes.

At const. P and T, suppose all the components are increased in the same proportion of their initial amounts. That is, the increase of 1st component is $n_1 \triangle x$, of the second component $n_2 \triangle x$, . . . etc, ith component will increase by $n_i \triangle x$ moles. Hence,

$$dn_1 = n_1 \triangle x, \quad dn_2 = n_2 \triangle x, \quad dn_i = n_i \triangle x, \ldots$$

Since G is an extensive property, its increase, $dG = G.\triangle x$. From equation (9.3), then

$$dG = \mu_1 n_1 \triangle x + \mu_2 n_2 \triangle x + \ldots + \mu_i n_i \triangle x + \ldots$$

$$\text{or} \quad G \triangle x = (\mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots) \triangle x.$$

$$\text{or} \quad G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots \qquad \ldots (9.4)$$

where G stands for the free energy of a system containing $n_1, n_2 \ldots$ gm. moles of the respective components.

Now complete differentiation of this equation (9.4) gives us,

$$dG = (\mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots) + (n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \ldots) \quad \ldots (9.5)$$

Subtracting equation (9.3) from equation (7.5)

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \ldots = 0 \quad \ldots (9.6)$$

We have thus three useful relations for chemical potentials with the composition of the system,

$$\left.\begin{aligned} (i)\ \ G &= \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots = \Sigma \mu n \\ (ii)\ \ dG &= \mu_1 dn_1 + \mu_2 dn_2 + \mu_3 dn_3 + \ldots = \Sigma \mu dn \\ (iii)\ \ 0 &= n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 + \ldots = \Sigma n d\mu \end{aligned}\right\} \quad \ldots (9.7)$$

These are commonly known as *Gibbs-Duhem* relations.

It must however be noted that the partial molal free energy (*i.e.*, chemical potential) is independent of the masses but is not independent of the composition of the system. Though it means the increase of G of the system per mole of the added substance but the increase depends upon the composition of the system. Thus if we add 1 gm mole of water to (*a*) one kgm of pure water and to (*b*) one kgm of a salt solution, the increase in Gibbs potential will not be exactly the same. To be more precise, it is the increase in the value of G at constant temperature and pressure from the addition of 1 mole of the component to an infinitely large quantity of the system such that the addition does not materially alter its composition. This also applies to other partial molal quantities, like partial molal volume, or partial entropy, etc.

If the system contains a pure material, then $G = \mu \times n$, or $\mu = G/n = \bar{G}$. In this instance, μ is the molar free energy.

9.3. General Concept of Chemical Potential

It has just been shown that the chemical potential μ is the partial molal free energy, $(dG/dn_i)_{P,T,n_1,n_2,\ldots}$, but it can be expressed as partial molal quantities of other thermodynamic functions though not at constant temperature and pressure.

We know, change in work-function,

$$dA = -PdV - SdT$$

so that $(\partial A/\partial T)_V = -S$; and $(\partial A/\partial V)_T = -P \quad \ldots (a)$

And also, $dG_{P,T} = dU + PdV - TdS$ . . . (b)

(see Sec. 6.2) $dA = dU - TdS - SdT$

$$\therefore\ dG_{P,T} = dA + PdV + SdT \quad \ldots (c)$$

The work-function (Helmholtz function) may be expressed as,

$$A = f(T, V, n_1, n_2, \ldots)$$

$$\text{or } dA = \left(\frac{\partial A}{\partial T}\right)_{V,n_1,n_2,\ldots} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n_1,n_2,\ldots} dV + \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2,n_3,} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1,n_3,} dn_2 + \ldots$$

$$\text{from (a)} = -SdT - PdV + \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2,n_3\ldots} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1,n_3\ldots} dn_2 + \ldots$$

Substituting this equation in (c) above,

$$dG_{P,T} = \left(\frac{\partial A}{\partial n_1}\right)_{T,V,n_2,n_3,\ldots} dn_1 + \left(\frac{\partial A}{\partial n_2}\right)_{T,V,n_1,n_3\ldots} dn_2 + \ldots \quad \ldots (9.8)$$

Comparing equations (9.2) and (9.8),

$$\left(\frac{\partial A}{\partial n_1}\right)_{V,T,n_2,n_3\ldots} = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2,n_3} = \mu_1$$

$$\left(\frac{\partial A}{\partial n_2}\right)_{V,T,n_1,n_3,} = \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1,n_3} = \mu_2, \text{ etc.}$$

The chemical potentials (μ) are the rate of change of work function, A, per mole at *constant volume and temperature*. These are not partial molal work functions as the pressure is not constant. It should be remembered,

$$\left(\frac{\partial A}{\partial n_1}\right)_{P,T,n_2,n_3,} = \bar{A}_1 \neq \mu_1.$$

Likewise the chemical potential can be expressed in terms of enthalpy, entropy, etc. For example, since $dH = TdS + VdP$,

$$\text{hence,} \quad \left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V \quad \ldots (d)$$

Again, $dG_{P,T} = dU - TdS + PdV$

and $dH = dU + VdP + PdV$

$$\therefore\ dG_{P,T} = dH - TdS - VdP \quad \ldots (e)$$

Expressing enthalpy, as,

$$H = f(P, S, n_1, n_2, \ldots)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_{S,n_1,\ldots} dP + \left(\frac{\partial H}{\partial S}\right)_{P,n_1,\ldots} dS + \left(\frac{\partial H}{\partial n_1}\right)_{P,S,n_2,\ldots} dn_1 + \left(\frac{\partial H}{\partial n_2}\right)_{P,S,n_1,\ldots} dn_2 + \ldots$$

$$\text{(from } d) = VdP + TdS + \left(\frac{\partial H}{\partial n_1}\right)_{P,S,n_2,\ldots} dn + \left(\frac{\partial H}{\partial n_2}\right)_{P,S,n_1} dn_2 + \ldots$$

from equation (*e*), by substitution,

$$dG_{P,T} = \left[\frac{\partial H}{\partial n_1}\right]_{P,S,n_2,\ldots} dn_1 + \left[\frac{\partial H}{\partial n_2}\right]_{P,S,n_1,\ldots} dn_2 + \ldots$$

Comparing with equation (9.3),

$$\mu_1 = \left[\frac{\partial H}{\partial n_1}\right]_{P,S,n_2,\ldots} ; \; \mu_i = \left[\frac{\partial H}{\partial n_i}\right]_{P,S,n_1,\ldots} \qquad \ldots (9.9)$$

The rate of change of enthalpy per mole at *constant entropy and pressure* equals chemical potential but is not the partial molal enthalpy as the temperature is not constant.

In the same way, it can be shown,

$$\mu_i = \left[\frac{\partial U}{\partial n_i}\right]_{S,V,n_1,\ldots} ; \; \mu_i = -T\left[\frac{\partial S}{\partial n_i}\right]_{U,V,n_1,\ldots} \qquad \ldots (9.10)$$

9.4. Effect of Temperature on Chemical Potential

The chemical potential of the *i*th component in a system,

$$\mu_i = \left(\frac{\partial G}{dn_i}\right)_{P,T,n_j} ; \text{ and hence } \left[\frac{\partial \mu_i}{\partial T}\right]_{P,n_j} = \frac{\partial^2 G}{\partial n_i dT}$$

$$\text{Again, } -S = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} ; \text{ and hence } -\left[\frac{\partial S}{\partial n_i}\right]_{P,T,n_j} = \frac{\partial^2 G}{\partial T \partial n_i}$$

$$\text{and } \left[\frac{\partial S}{\partial n_i}\right]_{P,T,n_j} = \bar{S}_i$$

Since dG is a perfect differential,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = -\bar{S}_i \qquad \ldots (9.11)$$

That is, the rate of change of chemical potential with temperature of a component is equal to its partial molal entropy, pressure remaining constant.

Application of Gibbs-Helmholtz relation gives

$$\mu_i = \bar{G}_i = \bar{H}_i - T\bar{S}_i \qquad \ldots (9.12)$$

From (9.11) $$\mu_i = \bar{H}_i + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j}$$

Multiplying by $(-1/T^2)$ and arranging,

$$\frac{-\mu_i}{T^2} + \frac{1}{T}\left(\frac{\partial \mu_i}{\partial T}\right) = \frac{-\bar{H}_i}{T^2}$$

$$\text{or} \quad \left[\frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)\right]_{P,n_j} = \frac{-\bar{H}_i}{T^2} \qquad \ldots (9.13)$$

This is similar to the Gibbs-Helmholtz relation for a closed system (Eqn 6.26.) and is often found to be very useful.

9.5. Effect of Pressure on Chemical Potential

Since $dG = VdP - SdT$, or $\left(\frac{\partial G}{\partial P}\right)_{T,n} = V$

Differentiating, $\frac{\partial^2 G}{\partial P \partial n_i} = \left(\frac{\partial V}{\partial n_i}\right)_{P,T,n_j} = \bar{V}_i$ (partial molal volume)

Again $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$; and hence $\frac{\partial^2 G}{\partial n_i \partial P} = \left[\frac{\partial \mu_i}{\partial P}\right]_{T,n_j}$

Hence, $$\left[\frac{\partial \mu_i}{\partial P}\right]_{T,n_j} = \bar{V}_i \qquad \ldots (9.14)$$

The rate of change of chemical potential of a component with pressure at constant temperature is equal to its partial molal volume.

If the system be one of ideal gases containing n moles, of which $n_1, n_2, n_3 \ldots$ are the numbers of moles of different gases, then, the volume of the system,

$$V = (n_1 + n_2 + n_3 + \ldots + n_i + \ldots)\,(RT/P)$$

$$\therefore \qquad \left(\frac{dV}{\partial n_i}\right)_{P,T,} = \frac{RT}{P}; \quad i.e., \quad \bar{V}_i = RT/P$$

So, from eqn (9.14); $\left(\dfrac{d\mu_i}{\partial P}\right)_{T,n_j} = \dfrac{RT}{P}$ . . . (9.15)

$$\therefore \qquad d\mu_i = RT\,d\,ln\,P \qquad \ldots (9.16)$$

But the partial pressure of the component $p_i = x_iP$, where x_i is the mol-fraction of the component; $x_i = n_i/\Sigma n$. In a given system x_i is constant, and

$$ln\,p_i = ln\,x_i + ln\,P$$

$$\text{or } d\,ln\,p_i = d\,ln\,P \qquad \ldots (9.17)$$

Substituting in (9.16); $d\mu_i = RTd\,ln\,p_i$

$$\text{or} \qquad \mu_i = RT\,ln\,p_i + \mu_i{}^{\circ}{}_{(p)}\,(\text{constant}) \qquad \ldots (9.18)$$

where the constant $\mu_i{}^{\circ}{}_{(p)}$ denotes the chemical potential of the component under unit pressure.

Since $p_i = x_iP$; hence $\mu_i = RT\,ln\,x_iP + \mu_i{}^{\circ}{}_{(p)}$

$$\text{or} \qquad \mu_i = RT\,ln\,x_i + \mu_i{}^{\circ}{}_{(x)}\,(\text{constant}) \qquad \ldots (9.19)$$

If the system contains a pure substance, $x_i = 1$, so that $\mu_i{}^{\circ}{}_{(x)} = \mu_i =$ molal free energy of the substance.

The same expression for chemical potential would apply to components present in solutions or mixtures in condensed phases. Because at eqm the chemical potential in the liquid or condensed phase will be the same as in the vapour phase at eqm hence .

$$\mu_i = RT\,ln\,p_i + \mu_i{}^{\circ}{}_{(p)}$$

Because in dilute solutions mol-fractions are proportional to molar concentrations C eqn, (9.19), may be changed to

$$\mu_i = RT\,ln\,C_i + \mu_i{}^{\circ}{}_{(c)} \qquad \ldots (9.20)$$

The chemical potentials for *ideal systems* can then be summarised :

$$\left.\begin{aligned} \mu_i &= RT\, ln\, p_i + \mu_i{}^{\circ}{}_{(p)} \\ \mu_i &= RT\, ln\, x_i + \mu_i{}^{\circ}{}_{(x)} \\ \mu_i &= RT\, ln\, C_i + \mu_i{}^{\circ}{}_{(c)} \end{aligned}\right\} \quad \ldots (9.21)$$

The way the chemical potential changes with pressure can be seen from the table below, for ideal gases at 25°C.

TABLE

P (atm)	0.1	0.5	1.0	2.0	10.0	20.0
$\mu-\mu^{\circ}$ (Cal)	−1355	−410	0	+410	+1355	+1762

Since the laws of ideal gases are also extended to ideal solutions, the relations of (9.21) will hold true in the latter also.

It must be remembered that the magnitude of chemical potential (*i.e.*, partial molal free energy) would depend upon the composition of the system. For a pure substance μ will have a constant value independent of the total mass and is identical with its molar free energy.

The equation (9.21) for chemical potential,

$$\mu_i = RT \ln p_i + \mu_i{}^{\circ}{}_{(p)}$$

is valid for ideal gases only, since it is derived by assumming $\bar{V}_i = RT/P$. In real gases, this is not permissible ; for $\bar{V_i}$ an expression from van der Waals' or some other equation of state has to be introduced. That would be a cumbrous and lengthy undertaking leading to unwieldy expressions for μ. It was Lewis (1901) who introduced a new function, **f**, called **fugacity,** to replace the pressure in the equation for chemical potential. The fugacity, in substituting the pressure, will include in it the imperfections of the real gases and yet retaining the form of the equation. We shall see that this gives us a computational advantage and is the outcome of the desire to keep the thermodynamic superstructure based on gas laws unravaged by deviations of real gases. It is an artificial concept for expressing the pressure and yet quite useful.

For real gases, $\mu_i = RT \ln \mathbf{f} + \mu_i{}^{\circ}{}_{(f)}$ . . . (9.22)

It is also common knowledge that real gases tend to behave ideally at very low pressures. That is,

$$Lt\ p \to 0,\ \mathrm{f}/p \to 1$$

Before we proceed any further with chemical potential and fugacity, it would be worthwhile to consider some aspects of different partial molal properties.

9.6. Apparent molal quantity

Consider a binary solution containing n_2 moles of solute dissolved in n_1 moles of solvent. The suffix 1 shall be used for solvent and 2 for solutes. If X denotes the value of a given property of the solution and X_1 and X_2 of the components, then in an ideal case,

$$X = n_1X_1 + n_2X_2$$

But in actual cases, such additivity does not hold true. The contribution per mole of the solute to that property of the solution may be expressed by ϕ_{x_2}. Then,

$$X = n_1X_1 + n_2\phi_{x_2}, \text{ or } \phi_{x_2} = \frac{X - n_1X_1}{n_2} \quad \text{..} (9.23)$$

This ϕ_{x_2} is called apparent molal property. Though it has little thermodynamic significance, nevertheless it is often quite useful in evaluation of true partial molal quantities of components of the solution.

Thus, apparent Gibbs potential or molal volume of the solute in the binary system would be given by

$$\phi_{G_2} = (G - n_1G_1)/n_2\ ;\quad \phi_{v_2} = (V - n_1V_1)/n_2$$

9.7. Determination of Partial Molal Quantities

Of the different methods used to find out partial molal quantities only two are mentioned here.

Graphical Method. The apparent molal property,

$$X = n_1\bar{X}_1 + n_2\phi_{x_2}$$

where X is an extensive property of the mixture (*i.e.*, solution) and $\bar{X}_1$ is the partial molal property of the solvent.

If the amount of the solvent n_1 be kept constant and the value of n_2 be changed, we shall obtain a series of values of ϕ_{x_2}. By differentiating X with respect to n_2 (at constant n_1),

$$\frac{dX}{dn_2} = \phi_{x_2} + n_2\,\frac{d(\phi_{x_2})}{dn_2} = \phi_{x_2} + \frac{d(\phi_{x_2})}{d\ln n_2}$$

or
$$\bar{X}_2 = \phi_{x_2} + \frac{1}{2.303}\cdot\frac{d(\phi_{x_2})}{d\log n_2} \qquad \ldots (9.24)$$

Now, if we plot the apparent molal property ϕ_{x_2} against $\log n_2$ the slope of the curve at a given point $\log n_2$ divided by 2.303 and added to the apparent molal property will give the value of the partial molal property (Fig. 9*a*).

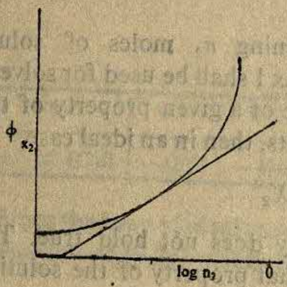

Fig. 9*a*
Graphical determination
partial molal quantity

Method of intercepts. This is a very useful and convenient method for the determination of the partial molal quantities.

If y denotes the mean value of the property to be studied per gm-molecule of the mixture (or solution), so that

$$y = \frac{X}{n_1 + n_2}\ ;\ i.e.,\ X = (n_1 + n_2)y$$

(n_1, n_2 are the gm-moles of the components in the mixture). At constant temperature and pressure and *at constant* n_1 (*i.e.*, constant amount of the solvent), if we differentiate with respect to n_2, then

$$\bar{X}_2 = \left[\frac{\partial X}{\partial n_2}\right] = y + (n_1 + n_2)\,\frac{dy}{dn_2} \qquad \ldots (9.25)$$

The mol-fraction of the solvent $N_1 = n_1/(n_1 + n_2)$

Hence, *at constant* n_1,

$$\frac{dN_1}{dn_2} = -\,\frac{n_1}{(n_1 + n_2)^2} = -\,\frac{N_1}{n_1 + n_2}$$

or
$$\frac{\partial y}{dN_1}\cdot\frac{dN_1}{dn_2} = -\,\frac{N_1}{n_1 + n_2}\cdot\frac{dy}{dN_1}$$

or $$\frac{dy}{dn_2} = -\frac{N_1}{n_1+n_2} \cdot \frac{dy}{dN_1}$$

Substituting this in equation (9.25),

$$\bar{X}_2 = y - N_1 \frac{dy}{dN_1} \qquad \ldots (9.26)$$

Since $\frac{dy}{dN_1}$ is not dependent on the way N_1 is computed, it is no longer necessary to assume n_1 as constant in equation (9.26).

The observed mean value of the property per mole, y, are plotted against *mol-fraction* of the solvent N_1, as the curve CD in Fig. 9*b*. Let the point L represent the mol-fraction of the solvent in the solution whose partial property is to be studied. Draw the line MLN parallel to N_1-axis and draw the tangent PLQ at the point L. Then the slope at L, is tan $\angle PLM$, or

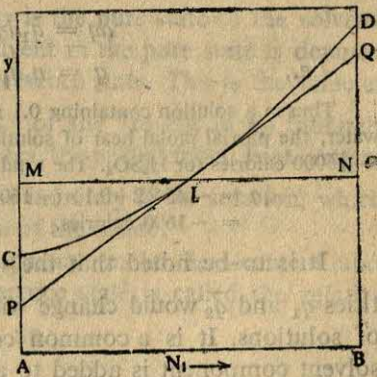

Fig. 9*b*. Partial mulal quantities from the method of intercepts

$$PM = N_1 \left[\frac{dy}{dN_1}\right]$$

Hence, $$\bar{X}_2 = y - N_1 \frac{dy}{dN_1} = AM - PM = AP$$

Similarly, it can be shown $\bar{X}_1 = BQ$

So, the partial molal quantities of both the components of the solution can be ascertained from the intercepts of the y-axis.

9.8. Partial molal heat of solution

If q quantity of heat be absorbed when n_1 mols of A are mixed with n_2 moles of B to form a homogenous solution, q is called the *total heat of solution*. If, in a given solution we add a small quantity Δn_1 moles of A (other factors remaining constant) and Δq heat be absorbed, then

$$\frac{\Delta q}{\Delta n_1} \approx \frac{dq}{dn_1} = \bar{q}_1$$

Obviously, $\bar{q}_1$ is the *partial molal heat of solution of A* in the *given* solution. This is also often named as the *differential heat of solution.* Similarly, $\bar{q}_2$, is the partial molal or differential heat of solution of B in the given solution.

When the partial molal heats of solution are known, the total heat of solution can be calculated, for

$$dq = \bar{q}_1 dn_1 + \bar{q}_2 dn_2$$

i.e.,

$$q = n_1\bar{q}_1 + n_2\bar{q}_2 \quad \ldots (9.27)$$

Thus in a solution containing 0.1 mole of sulphuric acid in 2.0 moles of water, the partial molal heat of solution are given as -45 calories for water and -16000 calories for H_2SO_4. The total heat of solution will be

$$\begin{aligned} q &= -45\times2+0.1\times(-16000) \\ &= -1690 \text{ calories.} \end{aligned}$$

It is to be noted that the values of the partial molal quantities $\bar{q}_1$ and $\bar{q}_2$ would change with variation of the concentration of solutions. It is a common convention that when the so-called solvent component is added to a solution, the heat-change occurring is called the *heat of dilution*.

Suppose n_1 moles of A (solvent) and n_2 moles of B form a solution to which n_1' moles of solvent is further added. Let $\bar{q}_1$ and $\bar{q}_2$ are the partial molal heats of solution of A and B in the original solution and $\bar{q}_1'$ and $\bar{q}_2'$ are the corresponding values in the final diluted solution. Then

$$q = n_1\bar{q}_1 + n_2\bar{q}_2$$

$$q' = (n_1 + n_1')\bar{q}_1' + n_2\bar{q}_2'$$

$$\therefore \Delta q_{\text{dil}} = q' - q = (n_1 + n_1')\bar{q}_1' + n_2\bar{q}_2' - n_1\bar{q}_1 - n_2\bar{q}_2$$

In the example given above, we have seen that the heat of solution of 0.1 mol H_2SO_4 in 2 mols of water is -1690 cal. What would be the quantity of heat absorbed if we add another mol of water to this solution? Given : in a solution of mol-fraction $N_2 = 0.033$, the partial molal heat of H_2SO_4 is -18500 cal. and that of water -20 cal.

The total heat of the final solution

$$q' = n_2'\bar{q}_2' + (n_1 + n_1')\bar{q}_1' = 0.1 \times (-18500) + 3 \times (-20) = -1910 \text{ cal.}$$

$$\therefore \text{ Heat of dilution} = -1910 - (-1690) = -220 \text{ cal.}$$

These thermal quantities can also be explained from a consideration of the molal heat-contents of the components.

9.9. Partial molal heat contents

The molal volume or the molal heat capacity can be directly measured, but it is not possible to determine the molal heat content directly. In measuring molal heat content $\bar{H}$, we have to refer to some standard state and then express it as whether it is less or greater than that in the chosen state. So far as the solvent is concerned, the reference or the standard state is the pure state of the solvent. The molal heat content of the solvent in the pure state is denoted by H_1°, the suffix (°) indicating reference state. This is the same as the partial molal heat content $\bar{H}_1^\circ$ of the solvent in an infinitely dilute solution. In the case of solutes, the partial molal heat-content $\bar{H}_2^\circ$ is its molal heat content at the infinitely dilute solution, which is recognised as the reference state of the solute.

The difference between the partial molal heat-content and its molal heat-content at the reference state is called the *relative molal heat content*, denoted by $\bar{L}$. So,

$$L_1 = H_1 - H_1^\circ\,; \qquad L_2 = H_2 - \bar{H}_2^\circ$$

Now, let H denote the heat-content of a solution formed from n_1 mols of A (solvent) and n_2 mols of B (solute). Let H_1°, H_2° be the molal heat contents of A and B respectively and q be the heat of solution. Then

$$q = H - n_1 H_1^\circ - n_2 H_2^\circ \qquad \ldots (9.28)$$

To the given solution, if we add a small quantity (dn_1) of A, then the partial molal heat-content of A in the given solution is

$$\bar{H}_1 = \left(\frac{\partial H}{\partial n_1}\right)_{n_2}$$

Further, the heat absorbed on addition of the solvent A to the solution per mole is

$$\frac{dq}{dn_1} = \bar{H}_1 - H_1^\circ$$

i.e., the increase in heat-content of the solution over the heat-content of the added substance. Or,

$$\bar{q}_1 = \bar{H}_1 - H_1^\circ = \bar{H}_1 - \bar{H}_1^\circ = \bar{L} \qquad \ldots (9.29)$$

That is, partial molal heat of solution of A is the relative molal heat content of A. This is also the *differential heat of dilution*.

Similarly, for ths solute, $\bar{L}_2 = \bar{H}_2 - \bar{H}_2^\circ$

In equation (9.28), we can substitute H as $n_1H_1 + n_2H_2$

and obtain
$$q = n_1H_1 + n_2H_2 - n_1\bar{H}_1^\circ - n_2\bar{H}_2^\circ$$
$$= n_1\bar{L}_1 + n_2\bar{L}_2 = L$$

which may be called the *total relative heat-content of the solution.*

9.10. Partial molal heat capacity

The heat-capacity C_P of a solution containing n_1 moles of A and n_2 moles of B is defined as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n_1,n_2} \quad \ldots (9.30)$$

where H is the heat-content of the solution.

The partial molal heat capacities may be expressed as

$$\bar{C}_{P_1} = \left(\frac{\partial C_P}{\partial n_1}\right)_{P,n_2} ; \; \bar{C}_{P_2} = \left(\frac{\partial C_P}{\partial n_2}\right)_{P.n_1}$$

so that, the total heat-capacity of the solution C_P would be

$$C_P = n_1\bar{C}_{P_1} + n_2\bar{C}_{P_2}$$

Differentiating (9.30),

$$\frac{\partial C_P}{\partial n_1} = \frac{\partial^2 H}{\partial T \partial n_1} ; \; i.e., \; \bar{C}_{P_1} = \frac{\partial^2 H}{\partial T \partial n_1}$$

But we know, $\bar{H}_1 = \dfrac{\partial H}{\partial n_1}$; or $\left(\dfrac{\partial \bar{H}_1}{\partial T}\right) = \dfrac{\partial^2 H}{\partial n_1 \partial T}$

$$\therefore \; C_{P_1} = \left(\frac{\partial \bar{H}_1}{\partial T}\right)$$

From equation (9.29). $\bar{L}_1 = \bar{H}_1 - \bar{H}_1^\circ$

$$\text{or} \quad \frac{\partial \bar{L}}{\partial T} = \left(\frac{\partial \bar{H}_1}{\partial T}\right) - \left(\frac{\partial \bar{H}_1^\circ}{\partial T}\right) = \bar{C}_{P_1} - \bar{C}_{P_1}^\circ$$

Where $\bar{C}_{P_1}{}^\circ$ stands for the molal heat capacity of the component in the standard state. That is, from a knowledge of the partial molal heat-capacities, it would be possible to measure, the change of the relative partial heat-content of a solution.

9.11. Partial Molal Volume

The partial molal volume is the change in volume obtained by adding 1 mole of a component to such a large volume of the solution that the change in concentration of the solution is negligible, the temperature and pressure remaining constant.

Suppose V litres of a solution is formed by dissolving 1 mole of a solute (mol. wt. M_2) in n_1 moles of solvent (mol. wt. M_1). Let the density of the solution be ρ gm-litre^{-1}.

Then $$\rho = (n_1M_1 + M_2)/V$$

or $$n_1 = (\rho V - M_2)/M_1$$

$$\therefore\ dn_1 = \frac{\rho dV + Vd\rho}{M_1}\ ;\ \text{hence}\ \left(\frac{dV}{dn_1}\right)_{P,T,n_2} = \frac{M_1}{\rho + V(\partial\rho/dV}$$

Since $c = 1/V$; $$V(\partial\rho/\partial V) = -\,c(\partial\rho/dc)$$

$$\therefore\ \text{Partial volume, } \bar{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{P,T,n_2} = \frac{M_1}{\rho - c(\partial\rho/\partial c)} \quad . . . (9.31)$$

Similarly $\bar{V}_2$ can also be expressed in a similar manner.

The densities (ρ) of solutions of different concentrations (c) are plotted against (c). Then $d\rho/dc$ is obtained from the tangent of the curve at the desired point. Substituting ρ and $d\rho/dc$ in eqn (9.31), the partial molar volume is obtained.

Example. The molar volume of pure water is 18 c.c. at 4°C and that of ethyl alcohol 58 c.c. If 1 mole of each are mixed together and if the mixture were ideal, then

$V_{id} = 18 + 58 = 76$ c.c. But, it is found that the volume of the mixture is 74.2 c.c. There is a considerable shrinkage. The volume of the mixture when different moles of alcohol are added to 1 mole of water are shown in Fig 9*c*. The slope of the curve at any point is the partial molar volume of alcohol.

The partial molar volumes as determined from above or from eqn (9.31) are shown in Fig. 9*d*.

The shrinkage occurs upon mixing when the forces of attraction between unlike molecules are greater than those between like molecules, as in this case of water and ethanol. The partial molal volumes would be usually less than the molar volumes of the pure components. If the intermolecular attractions are weaker, then expansion occurs on mixing ; the partial molal volumes would be greater than the molar volumes of the pure components. If the interactions between the like and the unlike molecules be the same (benzene and toluene), the partial molal volumes would be the same as the pure molar volumes. *i.e.* $V = n_1\overline{V}_1^0 + n_2\overline{V}_2^0$.

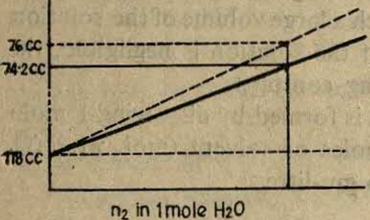

Fig 9*c*. V_{min} *vs* n_2

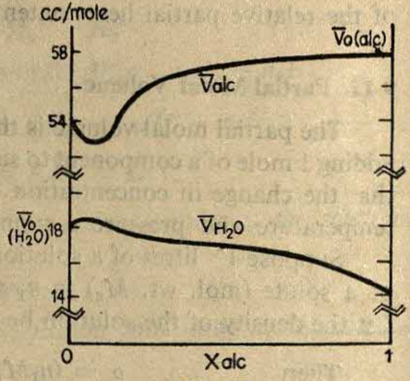

Fig 9*d*

Problems

1. Derive : $\Sigma N_i\,(d\mu_i - \overline{V}_i\,dP - \overline{S}_i\,dT) = 0$

Show that the partial molal free energy of a component in the two phases in equilibrium will be the same.

2. At 25°C, the volume of a solution of NaCl per Kg of water is given by $V = 1003 + 16.4\,m + 2.5m^2 - 1.2\,m^3$ provided the concentration is more than 0.3 molal.

The molar volume of pure water, $\overline{V}_1 = 18.07$ c.c./mole at 25°C. Show that in a 0.5 molal solution, $\overline{V}_2 = 18.00$ c.c. Find out also the apparent molal valume, ϕ_{v2}.

3. The apparent molar heat capacity of a non-electrolyte in water is given by $\phi_{c2} = 152 + 1.2\ m - 0.05\ m^2$ cal/deg.-mole where m is the molality of the solution. Calculate the heat-capacity of 1.0 molal solution in water.

4. Show that in a chemical equilibrium, the total chemical potentials of the reactants and of the products are equal.

5. Show that (*a*) the concentration of oxygen in sea-water remains unaltered as long as the partial pressure of oxygen in the atmosphere and temperature remain fixed ; (*b*) the ratio of concentration of iodine between water and benzene at a given temperature is constant.

CHAPTER 10

FUGACITY AND ACTIVITY

FUGACITY

10.1. The escaping tendency

If a system or a part of a system be at a temperature higher than that of its surroundings, then the heat-energy would escape from the former to the latter. The higher the temperature, the greater is the tendency of the heat-escape. On the other hand, if the temperature of a given part is lower than that of its surroundings, heat energy will flow into it escaping from the surrounding parts. Temperature is thus a measure of the escaping tendency of the heat-energy. If the system be in thermal equilibrium with its surroundings, *i.e.*, at the same temperature, then the escaping tendencies of heat in different parts would be the same.

This idea was extended to the material substances by Lewis. Suppose there is a system containing a substance in two different phases *A* and *B* at the same temperature, then in each phase the substance has a tendency to flow out or escape from its own phase. Actually the substance will escape from the phase *A* to the phase *B* if the escaping tendency in phase *A* is greater than that in phase *B*. Similarly, if the escaping tendency in phase *B* is greater than that in phase *A*, then it cannot escape from phase *A*, rather the matter will pass from phase *B* to *A*. Some illustrations may explain it clearly.

Suppose a closed vessel contains some liquid water and its vapour at 100°C and at one atmosphere. In these circumstances, the phases are in equilibrium. The vapour that might condense into the liquid phase would be the same as the liquid vaporising. The escaping tendencies of water in the liquid and in the vapour phases are equal, though the quantities in the two phases need not be so. Now, if at one atmosphere, the temperature is raised to 101°C, the water molecules will have a greater tendency to escape from the liquid phase and the latter would disappear in favour of the gaseous phase. Similarly, if at the same pressure the temperature is lowered than 100°C, the gaseous H_2O molecules would condense or the escaping tendency of H_2O molecules in the gas-phase will be greater than that in the liquid phase. The gas-phase then will disappear slowly.

Consider again a system containing a solid, say sugar, in contact with its solution, at a given temperature. Sugar is present in two phases, the solid phase and the solution phase. If the solution is unsaturated, the solid would disappear into the solution, showing that the escaping tendency is greater in the solid phase. If the solution is just saturated, the escaping tendency of the sugar from the solution will just balance its escaping tendency from the solid phase. As a result the amount of sugar escaped from one phase would be recovered by the return of an equal amount from the other phase. If the solution be supersaturated, then the escaping tendency of sugar in the solution phase would be higher and it would escape from the solution to the solid phase till the escaping tendencies in the two phases are equal.

Again, suppose two aqueous solutions of a substance, say glucose, of different concentrations are taken in two beakers *A* and *B* and kept inside a closed space at a constant temperature (Fig. 10*a*).

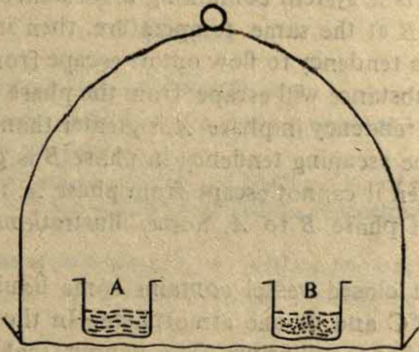

Fig. 10*a*

It is our experience that water would slowly vaporise from the dilute solution and the solution with the higher concentration would gradually be diluted. This shows that the escaping tendency of water in the more dilute solution is higher than that in the other. In fact, this principle is involved in the dehydration of substances carried out in the common dessicators.

Thus, we conclude that every substance has a tendency to escape from the phase in which it exists. Unless the escaping tendency is counter-balanced by the tendency of the molecules to return to the given phase from another co-existing phase, the phase in which the escaping tendency is greater will disappear in favour of the phase of smaller escaping tendency. We can thus say, that if a substance be distributed in several phases in a system which has attained thermodynamic equilibrium, then the escaping tendency of the substance in the different phases will be the same. It must be remembered that we are not comparing the escaping tendency of one substance with that of another but we are comparing the escaping tendencies of the same substance in different phases. The escaping tendency of a system as a whole has no meaning.

We have seen that temperature is a measure of the escaping tendency of heat. It is now necessary to find some function to make quantitative measurement of the escaping tendency of a substance from a phase.

10.2. The escaping tendency and the molal free energy

Consider a system containing water and its vapour in equilibrium at a temperature T. Let an infinitesimal amount (Δn moles) of liquid water be vaporised under conditions of equilibrium. Then, the free energy change would be

$$\Delta G_{eqm} = 0$$

From the Gibbs-Duhem relations (9.7), at equilibrium

$$\mu_I(-\Delta n) + \mu_{II}(\Delta n) = \Delta G = 0$$

$$\text{or} \quad \mu_I = \mu_{II}\,; \quad i.e., \quad \bar{G}_I = \bar{G}_I{}' \qquad \ldots (10.1)$$

The suffix I is for one phase and suffix II for the other phase.

If the temperature is lowered, the process of vaporisation is opposed and $\bar{G}_{vap} > \bar{G}_{liq}$; *i.e.*, $\Delta\bar{G} = \bar{G}_{vap} - \bar{G}_{liq} > 0$

On the other hand, if the temperature be increased, the vaporisation is enhanced ; the free energy of the liquid is greater than that of the vapour, $\bar{G}_{liq} > \bar{G}_{vap}$; *i.e.*, $\Delta\bar{G} = \bar{G}_{vap} - \bar{G}_{liq} < 0$

It shows that if the partial molal free energy of a component is greater in one phase than in another, the component would escape from the former to the latter. The partial molal free energy (or chemical potential) is thus a measure of the escaping tendency.

Let us take another example. Suppose under conditions of eqm, iodine is distributed between water and chloroform in a system. Imagine a transfer of an infinitesimal quantity of iodine ($\triangle n$ moles) from chloroform layer to aqueous layer, then, at eqm.,

$$\mu_I(\triangle n) + \mu_{II}(-\triangle n) = \triangle G_{eqm} = 0$$

or $$\mu_I = \mu_{II}$$

The suffixes I and II stand for aqueous and chloroform phases.

Hence, *under conditions of equilibrium, the chemical potential (or partial molal free energy) of a component in every phase must be the same.*

This indeed is the criterion for phase equilibrium.

$$\mu_i' = \mu_i'' = \mu_i'''$$

where *i* indicates the component in the system and the primes refer to different phases.

The molal free energy would be a quantitative measure of the escaping tendency and indeed it proves satisfactory in comparing escaping tendencies in many cases. But there are some inconveniences also in its use. We know, from eqn (9.14)

$$\left(\frac{d\mu}{\partial P}\right)_{T,n} = \bar{V}$$

At low pressures the chemical potential decreases rapidly as the pressure decreases. If μ is finite at 1 atm, it will approach a very high negative value at very low pressures. On the other hand, if μ has a finite value at low pressures then it would have high positive values at ordinary or higher pressures. For this reason, a new property called *fugacity* (**f**) has been proposed by G. N. Lewis and is now in widespread use for all gases.

10.3. Fugacity

Since the molar free energy could be a measure of the escaping tendency, then it is reasonably expected that any other function or property to which molar free energy is simply or monotonically related may serve as a measure of the escaping tendency. Now, for a mole of an *ideal* gas,

$$\bar{G} = \bar{G}^0 + RT \ln P \qquad \ldots (10.2)$$

or $$\mu = \mu^0_{(P)} + RT \ln P \qquad \ldots (10.3)$$

If there be a mixture of ideal gases, partial molal free energies would be similar,

$$\bar{G}_1 = \bar{G}_1{}^0 + RT\, ln\, p_1 \qquad \ldots (10.4)$$

$$\mu_1 = \mu^0{}_{1(p)} + RT\, ln\, p_1$$

or

$$d\mu_1 = RTd\, ln\, p_1 \qquad \ldots (10.5)$$

To maintain same structure for the expression of free energy of *real* gases, it was proposed, to replace the pressures (P) by fugacities (f) in the corresponding equations (Sec. 9-5).

$$\bar{G}_1 = \bar{G}_1{}^0 + RT\, ln\, \mathrm{f}_1 \qquad \ldots (10.6)$$

$$\text{or} \quad \left.\begin{aligned} dG_1 &= RT\, d\, ln\, \mathrm{f}_1 \\ d\mu_1 &= RT\, d\, ln\, \mathrm{f}_1 \end{aligned}\right\} \qquad \ldots (10.7)$$

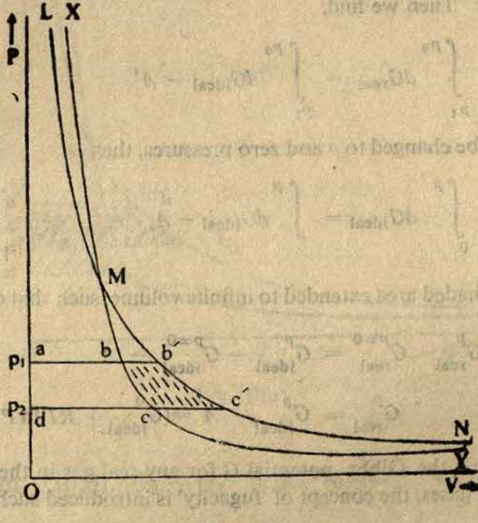

Fig. 10*b*

If vapours and gases behaved ideally, pressure could be accepted as a measure of free energy and hence of escaping tendency. But since we deal with real gases, the function fugacity would be a measure of the escaping tendency of a substance and it would include the departure from ideal state in case of real gases.

We may attempt to understand more clearly the term fugacity by graphical representation. In fig. 10*b*, let *LMN* and *XMY* represent the *P-V* isothermals for an ideal gas and a real gas respectively. As the pressure tends to zero, the two curves approach each other.

Suppose at a constant temperature, a given mass of gas changes its pressure from p_1 to p_2, the change in the Gibbs potential will be given by,

$$dG = VdP$$

This relation would be true for all gases, ideal or real. From the figure, we see, that

$$\int_{p_1}^{p_2} dG_{\text{ideal}} = \int_{p_1}^{p_2} VdP = \text{area } ab'c'd$$

And
$$\int_{p_1}^{p_2} dG_{\text{real}} = \int_{p_1}^{p} VdP = \text{area } abcd$$

There is a difference between the two areas and let the difference (shaded area) be denoted by A' Then we find,

$$\int_{p_1}^{p_2} dG_{\text{real}} = \int_{p_1}^{p_2} dG_{\text{ideal}} - A'$$

If the limits be changed to p and zero pressures, then

$$\int_{0}^{p} dG_{\text{ideal}} = \int^{p} dG_{\text{ideal}} - A$$

where 'A' is the shaded area extended to infinite volume, such that $G^{p=0}_{\text{ideal}} = G^{p=}_{\text{real}}$

Integrating $G^{p}_{\text{real}} - G^{p=0}_{\text{real}} = G^{p}_{\text{ideal}} - G^{p=0}_{\text{ideal}} - A$

or
$$G^{p}_{\text{real}} = G^{p}_{\text{ideal}} - A = (G^{0}_{\text{ideal}} + RT \ln P) - A$$

In order to express the Gibbs potential G for any real gas in the same form as that for the ideal gases, the concept of 'fugacity' is introduced such that

$$G^{p}_{\text{real}} = G^{0}_{\text{ideal}} + RT \ln \mathrm{f}$$

i.e.
$$RT \ln \mathrm{f} = RT \ln P - A$$

or
$$\mathrm{f} = P.e^{-\frac{A}{RT}}$$

which gives us a quantitative definition of fugacity.

'A' is a measure of the departure from ideality and it varies from point to point. In other words, for every pressure P in the curve XMY (real gas) there would be a corresponding fugacity 'f' in the curve LMN (ideal gas). Let b, c, in fig. 10*c* denote two points in the isothermal *XMY* of the real gas and let *b'* and *c'* denote the corresponding fugacities $\mathbf{f}_1$ and $\mathbf{f}_2$ in the ideal gas isothermal *LMN*. Then the area *a'b'c'd'* and *abcd* would be equal, both being separately equal to $\triangle G$. Hence for the real gas,

$$dG = \text{area } a'b'c'd' = RT \ln \frac{\mathbf{f}_1}{\mathbf{f}_2}.$$

We thus find that the advantage of the introduction of fugacity is that we can use the perfect gas expression for the Gibbs potential (G) and also for other expressions derived from it, and it covers the corrections necessary for real gases.

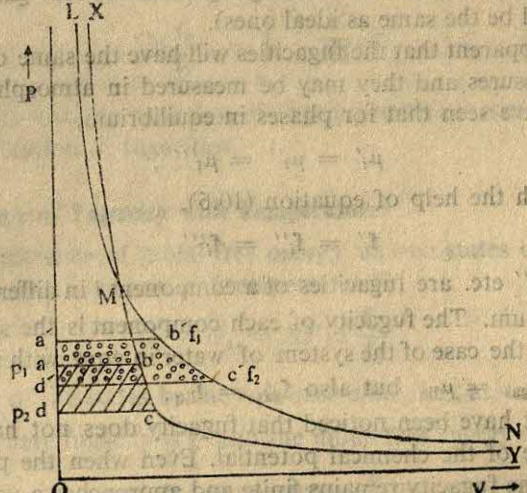

Fig. 10*c*

$$\text{From eqn (10.6)},\ G_2 - G_1 = RT \ln \frac{\mathbf{f}_2}{\mathbf{f}_1} \qquad \ldots (10.8)$$

where $\mathbf{f}_1$ and $\mathbf{f}_2$ are the fugacities of the gas at two pressures. By means of $\triangle G$ (*i.e.*, $G_2 - G_1$) we can find out the ratio of the fugacities ($\mathbf{f}_2/\mathbf{f}_1$) only. So, in order to put concrete values, it is necessary to define a standard value of the fugacity at a given reference state. For an ideal gas,

$$G_2 - G_1 = RT \ln \frac{P_2}{P_1} \quad \text{and also} \quad G_2 - G_1 = RT \ln \frac{\mathbf{f}_2}{\mathbf{f}_1}$$

i.e., in ideal gases, the fugacities are proportional to the pressures.

For convenience, the fugacities are also taken to be equal to the pressures in ideal gases. That is,

$$\mathbf{f}/P = 1 \quad \text{(in } \textit{ideal} \text{ gases)}$$

In *real* gases, $\mathbf{f}_1/\mathbf{f}_2 \neq P_1/P_2$.

But if the pressures be made very low, the real gases would behave ideally. Hence, at very low pressures even for real gases,

$$Lt_{P\to 0}\,; \quad \mathbf{f} = P$$

This is why it would be desirable to take the low pressure state as the *reference state* for measuring fugacities for real gases, (where they would be the same as ideal ones).

It is apparent that the fugacities will have the same dimensions as the pressures and they may be measured in atmospheric units.

We have seen that for phases in equilibrium,

$$\mu_i' = \mu_i'' = \mu_i''' ,$$

so with the help of equation (10.6),

$$\mathbf{f}_i' = \mathbf{f}_i'' = \mathbf{f}_i''' \qquad \ldots (10.9)$$

where $\mathbf{f}'$, $\mathbf{f}''$ etc. are fugacities of a component i in different phases at equilibrium. The fugacity of each component is the same in all phases. In the case of the system of water in eqm with its vapour, not only $\mu_{\text{gas}} = \mu_{\text{liq}}$ but also $\mathbf{f}_{\text{gas}} = \mathbf{f}_{\text{liq}}$.

It must have been noticed that fugacity does not have the inconvenience of the chemical potential. Even when the pressure is decreased the fugacity remains finite and approaches a value equal to the pressure itself when the pressure is very low.

This idea of fugacity may also be extended to the *solid or liquid states* of matter. At any given temperature, every solid or liquid has a definite vapour pressure. The condensed state (solid or liquid) is in equilibrium with its vapour and, therefore, the escaping tendencies in the vapour phase and the condensed phase must be equal to one another. The equation (10.6) therefore predicts that the fugacities in the condensed phase and the vapour phase must be the same at a given temperature, the reference state being the same. Very often, the vapour pressures of solids (or liquids) are low ; in such cases the fugacities may be measured by their vapour pressures. When the vapour pressures are high, the fugacities are to be determined by methods employed in cases of real gases, described later.

FUGACITY OF A PURE SUBSTANCE

10.4. Change of fugacity with pressure.

When $\bar{V}$ is the molar volume of a gas at temperature T, we have,

$$dG = \bar{V}dP$$

and from equation (10.7), $dG = RTd\ln \mathbf{f}$

$$\text{or} \qquad \left[\frac{\partial \ln \mathbf{f}}{\partial P}\right]_T = \frac{\bar{V}}{RT} \qquad \ldots (10.10)$$

$$\text{or} \qquad \ln \frac{\mathbf{f}_2}{\mathbf{f}_1} = \int_{P_1}^{P_2} \frac{\bar{V}}{RT} dP \qquad \ldots (10.11)$$

This relation for the variation of fugacity with pressure is useful in the calculation of fugacities.

10.5. Change of Fugacity with Temperature

The difference of molal free energy at two states of a gas at different pressures at constant temperature T,

$$\bar{G}_2 - \bar{G}_1 = RT \ln \frac{\mathbf{f}_2}{\mathbf{f}_1}$$

If one of the states be the *reference state, i.e.*, at very low pressure (p^0) where fugacity is $\mathbf{f}^0$ and the molal free energy $\bar{G}^0$, then

$$\bar{G} - \bar{G}^0 = RT \ln \frac{\mathbf{f}}{\mathbf{f}^0}$$

$$\text{or} \qquad R \ln \mathbf{f} - R \ln \mathbf{f}^0 = \frac{\bar{G}}{T} - \frac{\bar{G}^0}{T}$$

Differentiating this with respect to temperature, at constant pressure,

$$R\left[\frac{\partial \ln \mathbf{f}}{\partial T}\right]_P - R\left[\frac{\partial \ln \mathbf{f}^0}{\partial T}\right]_{P^0} = \left[\frac{\partial(\bar{G}/T)}{\partial T}\right]_P - \left[\frac{\partial(\bar{G}^0/T)}{\partial T}\right]_{P^0}$$

Since $\mathbf{f}^0$, at very low pressures, is equal to the pressure (P^0) and $\left(\frac{\partial \ln P^0}{\partial T}\right)_{P^0}$ at constant pressure will be zero,

$$Lt_{P \to 0}, \quad \left(\frac{\partial \ln \mathbf{f}^0}{\partial T}\right)_{P^0} = \left(\frac{\partial \ln P^0}{\partial T}\right)_{P^0} = 0$$

$$\therefore\ R\left(\frac{\partial \ln f}{\partial T}\right)_P = \left(\frac{\partial(\bar{G}/T)}{\partial T}\right)_P - \left(\frac{\partial(\bar{G}^0/T)}{\partial T}\right)_P$$

$$= \frac{1}{T}\left(\frac{\partial \bar{G}}{\partial T}\right)_P - \frac{\bar{G}}{T^2} - \frac{1}{T}\left(\frac{\partial \bar{G}^0}{\partial T}\right)_P + \frac{\bar{G}^0}{T^2}$$

$$= -\frac{1}{T^2}[T\bar{S} + \bar{G}] + \frac{1}{T^2}[T\bar{S}^0 + \bar{G}^0]$$

$$= -\frac{\bar{H}}{T^2} + \frac{\bar{H}^0}{T^2} = \frac{\bar{H}^0 - \bar{H}}{T^2},$$

in which $\bar{H}^0$ and $\bar{H}$ are the heat-contents of the vapour in the ideal state and in the given state. If the given state be a condensed state $\bar{H}^0 - \bar{H}$ may be called the ideal heat of vaporisation. Rewriting,

$$\left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{\bar{H}^0 - \bar{H}}{RT^2} \qquad \ldots (10.12)$$

which gives the variation of fugacity with temperature.

10.6. Calculation of Fugacity

Some of the different methods employed for the determination of fugacity are considered here.

(a) By graphical method : Suppose at a given temperature and pressure, V and V_i denote the molal volumes of a real and an ideal gas. Let the difference between these two be denoted by α, then

$$\alpha = V_i - V = \frac{RT}{P} - V$$

or $$\alpha dP = RTd\ln P - VdP$$

$$= RTd\ln P - RTd\ln f, \text{ [From Eqn 10.10]}$$

i.e., $$d\ln f = d\ln P - \frac{\alpha}{RT}dP$$

or $$\ln f = \ln P - \frac{1}{RT}\int_0^P \alpha dP \qquad \ldots (10.13)$$

or $$f = Pe^{-\frac{1}{RT}\int_0^P \alpha dP} \qquad \ldots (10.14)$$

To evaluate $\int_0^P \alpha dP$, the experimentally derived values of α (from molar volumes) are plotted against P, as in Fig. 10(d). The area under the curve from the given pressure P to the origin would give the value of the integrand. The substitution of this value in equation (10.13) enables us to calculate the value of the fugacity.

Since at very low pressures f/P becomes unity, *i.e.*, $\ln \frac{f}{P} = 0$, $\frac{\alpha}{RT}$ may also be plotted against pressure and then integrating from zero pressure to the pressure P, we can find the value of f with equation (10.14).

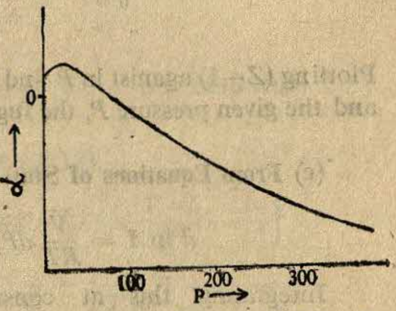

Fig 10(d). Graphical method for det. of fugacity.

Approximation : In the pressure range from zero to 1 atmosphere, 'α' virtually remains constant. The equation (10.13) may then be written as,

$$\ln f = \ln P - \frac{\alpha P}{RT}$$

i.e., $$\frac{f}{P} = e^{-\alpha P/RT} \approx \left(1 - \frac{\alpha P}{RT}\right)$$

or $$\frac{f}{P} = \frac{RT - \alpha P}{RT} = \frac{P\bar{V}}{RT} \approx \frac{P\bar{V}_i}{RT} = \frac{P}{P_{id}} \quad \ldots (10.15)$$

That is, the observed pressure P is the geometric mean of the ideal pressure and fugacity. Since P and P_{id} are known, f can be calculated.

The ratio of fugacity to the real pressure is called the fugacity coefficient, γ.

$$\gamma = f/P = \frac{P}{P_{id}} = \frac{P\bar{V}_i}{RT} \quad \ldots (10.16)$$

(b) From Compressibility factor : The non-ideal behaviour of gases is often expressed with the help of compressibility factor, Z, such that $Z = P\bar{V}/RT$.

$$\text{Now, } \alpha = \bar{V}_{id} - \bar{V} = \frac{RT}{P} - \bar{V} = \frac{RT}{P}\left(1 - \frac{P\bar{V}}{RT}\right) = \frac{RT}{P}[1 - Z]$$

or $$\frac{\alpha}{RT} = \frac{1 - Z}{P}$$

Substituting this in equation (10.13).

$$\ln \mathbf{f} = \ln P - \int_0^P \frac{1-Z}{P}\, dP = \ln P + \int_0^P (Z-1)\, d \ln P \quad \ldots (10.17)$$

Plotting $(Z-1)$ aganist $\ln P$ and integrating between zero pressure and the given pressure P, the fugacity can be evaluated.

(c) From Equations of State : For one mole of a real gas,

$$d \ln \mathbf{f} = \frac{\overline{V}}{RT}\, dP, \qquad \text{(From eqn 10.10)}$$

Integrating this at constant temperature between two pressures P and P' when fugacities are $\mathbf{f}$ and $\mathbf{f}'$;

$$\ln \frac{\mathbf{f}}{\mathbf{f}'} = \frac{1}{RT} \int_{P'}^{P} V dP$$

If the pressure P' be very low, say equal to P^0, where the gas behaves almost ideally, then

$$\ln \frac{\mathbf{f}}{\mathbf{f}^0} = \frac{1}{RT} \int_{P^0}^{P} V dP = \frac{1}{RT}\left(PV - P^0V^0 - \int_{V^0}^{V} PdV \right)$$

where V^0 is the infinitely large molal volume at very low pressure P^0.

$$\ln \mathbf{f} = \ln \mathbf{f}^0 + \frac{1}{RT}\left(PV - P^0V^0 - \int_{V^0}^{V} PdV \right)$$

Since at low pressures $P^0V^0 = RT$, and further $\mathbf{f}^0 = P^0$,

$$\ln \mathbf{f} = \ln P^0 + \frac{1}{RT}\left[PV - RT - \int_{V^0}^{V} PdV \right] \quad \ldots (10.18)$$

The integrand, $\int_{V^0}^{V} PdV$, may now be evaluated with an equation of state.

If the gas be a van der Waals' one, then

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\text{or} \qquad \int_{V^0}^{V} PdV = \int_{V^0}^{V} \frac{RT}{V-b}\,dV - \int_{V^0}^{V} \frac{a}{V^2}\,dV$$

$$= RT \ln \frac{V-b}{V^0-b} + \frac{a}{V} - \frac{a}{V^0}$$

$$\approx RT \ln \frac{V-b}{V^0} + \frac{a}{V}, \ [\because V^0 \text{ is infinitely large}].$$

Substituting this in equation (10.18),

$$\ln \mathrm{f} = \ln P^0 + \frac{1}{RT}\left[PV - RT - RT \ln \frac{V-b}{V^0} - \frac{a}{V} \right]$$

$$= \ln P^0 + \frac{1}{RT}\left[\frac{RTb}{V-b} - \frac{a}{V} - RT \ln \frac{V-b}{V^0} - \frac{a}{V} \right]$$

$$\left[\because PV - RT = b\left(P + \frac{a}{V^2}\right) - \frac{a}{V} = b\frac{RT}{V-b} - \frac{a}{V} \right]$$

$$\text{So,} \quad \ln \mathrm{f} = \ln P^0 + \frac{b}{V-b} - \ln \frac{V-b}{V^0} - \frac{2a}{RTV}$$

$$= \ln \frac{P^0V^0}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV}$$

$$= \ln \frac{RT}{V-b} + \frac{b}{V-b} - \frac{2a}{RTV} \qquad \ldots (10.19)$$

It is thus possible to calculate the fugacity from a knowledge of the van der Waals' constants and the volume of the gas.

Example : An example of a simple calculation of fugacity, say that of water vapour at 298°K, may be recorded here. The vapour pressure of water at this temperature is 23.73 mm (= 0.03122 atm).

Consider the change in thermodynamic potential when 1 gm-mol of liquid water is changed into vapour under 1 atmosphere *isothermally and reversibly*. We may imagine that first 1 mole of liquid is changed into vapour in equilibrium (p = 0.03122 atm) and then the pressure of the vapour is raised to 1 atmosphere. The changes in G would be

(I) $\triangle G_{\mathrm{I}}\,(H_2O_{\mathrm{liq}} \rightarrow H_2O_{\mathrm{v\,p.}\,=\,0{\cdot}03122}) = 0$

(II) $\triangle G_{\mathrm{II}}\,(H_2O_{\mathrm{vap.}\ P\,=\,0{\cdot}03122 \rightarrow P\,=\,1}) = RT \ln \dfrac{1}{0.03122} = 2054$ cal

(III) $\triangle G_{\mathrm{III}}$ (Correction for non-ideality) = 1.1 cal (Rossini, 1939)

$\therefore$ Net $\triangle G$ = 2054 + 1.1 = 2055.1 cal

This means that the molal thermodynamic potential of water vapour at 1 atmosphere is 2055.1 calories greater than that of liquid water.

But, the fugacity of water vapour in equilibrium ($p = 0.03122$ atm) is the same as that of liquid water.

$$G - G^\circ = RT \ln \frac{f}{1} = RT \ln f$$

where G and G^0 are the thermodynamic potentials of water vapour at fugacity f and at standard state.

$$\text{or} \quad RT \ln f = -2055.1$$

$$\text{or} \quad \log f = \frac{-2055.1}{2.303 \times 1.98 \times 298} \quad \text{or} \quad f = 0.03117 \text{ atm.}$$

10.7. Fugacity of a component in a solution

In the case of homogeneous mixtures or solutions the fugacity of a component is expressed, in the same form as for a pure substance, in terms of partial molal free energy ($\bar{G}$). So, from eqn (10.6),

$$\bar{G}_i = RT \ln f_i + \bar{G}_i^\circ \text{ (constant)} \qquad \ldots (10.20)$$

$$\text{or} \quad \mu_i = RT \ln f_i + \mu_i^\circ \qquad \ldots (10.21)$$

$$\text{Differentiating,} \quad d\bar{G}_i = RT\, d \ln f_i \qquad \ldots (10.22)$$

$$\text{or} \quad d\mu_i = RT\, d \ln f_i \qquad \ldots (10.23)$$

The variations of the fugacity of the component with pressure, and with temperature would be similar to those observed for pure gases as in sections (10.4 and 10.5) except that partial molal quantities are involved. The relations are,

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_{T,N} = \frac{\bar{V}_i}{RT}$$

where $\bar{V}_i$ is the [partial molal volume of the component i.]

$$\text{or,} \quad \left(\frac{\partial \ln f_i}{\partial T}\right)_{P,N} = \frac{\bar{H}_i^\circ - \bar{H}_i}{RT^2}$$

[where $\bar{H}_i^\circ$ and $\bar{H}^\circ$ are the molal heat content in pure state and partial molal heat content of the component in the mixture.]

The relations mentioned above take a simpler form in the cases of ideal mixtures or ideal solutions.

10.8. Ideal Solutions

In a mixture of benzene and toluene or of ethylene bromide and propylene bromide, it is found that the total volume of the mixture is practically additive of the volumes of the constituents. This is also true of other extensive properties such as free-energy, heat-capacity, etc. But in a mixture of water and alcohol, we find there are considerable deviations from the additive quantities of volumes or free-energies of the components. The mixtures or solutions which exhibit additive characters in the properties of the components are regarded as *ideal ones*. It is generally found that non-polar substances of similar chemical composition usually form ideal solutions.

An ideal solution (gaseous, liquid or solid) is defined as one in which the fugacity of each component is proportional to its mol-fraction at all temperatures and pressures and over the entire range of concentrations.

To illustrate, suppose n_1 gm-moles of A and n_2 gm-moles of B form an ideal solution. Then, mole-fraction of A and B are

$$\frac{n_1}{n_1+n_2} = N_1, \quad \frac{n_2}{n_1+n_2} = N_2$$

By definition, the fugacity of A, $\mathbf{f}_1 = \mathbf{f}_1^\theta N_1$

and the fugacity of B, $\mathbf{f}_2 = \mathbf{f}_2^\theta N_2$

If there be several components in the solution, then the fugacity of the ith component, $\mathbf{f}_i = \mathbf{f}_i^\theta N_i$ . . . (10.24)

The relation will hold true over the whole range of concentration. Hence it will be true, when $N_i = 1$, *i.e.*, in the case of a pure component,

$$\mathbf{f}_i = \mathbf{f}_i^\theta N_i = \mathbf{f}_i^\theta \qquad [\because N_i = 1]$$

Thus, $\mathbf{f}_i^\theta$ stands for the fugacity of the pure component in the *same state* (gas, liquid or solid) in which it exists in the mixture and at the same temperature and pressure.

(i) Now, from eqn (10.20), at a constant temperature,

$$\mu_i = RT \ln \mathbf{f}_i + \mu_i^0 = RT \ln \mathbf{f}_i^\theta N_i + \mu_i^0 \quad . . . (10.25)$$

$$\text{So, } d\mu_i = d\overline{G}_i = RT\, d \ln N_i = \frac{RT}{N_i}\, dN_i \quad . . . (10.26)$$

$$\therefore \quad \frac{\partial \mu_i}{\partial N_i} = \frac{\partial \overline{G}_i}{\partial N_i} = \frac{RT}{N_i} \quad . . . (10.27)$$

Consider two different solutions containing the component *i* in concentrations of N_i and N_i' mole-fractions, then

$$\mu_i - \mu_i' = RT \ln \frac{N_i}{N_i'}$$

If one of the solutions be such that $N_i' = 1$, (*i.e.*, pure component) then $\mu_i \doteq \mu_i^0$, so

$$\mu_i = \mu_i^0 + RT \ln N_i \qquad \ldots (10.28)$$

or $$\bar{G}_i = \bar{G}_i^0 + RT \ln N_i \qquad \ldots (10.29)$$

It represents the most important character of the ideal solutions. It means *the increase in the free energy of a component over that in the pure state is proportional to the logarithm of the mole-fraction of the same component in an ideal solution.*

From equation (10.29), for all the components in an ideal solution, $$\triangle G_{\text{mix}} = RT\ \Sigma N_i\, RT \ln N_i \qquad \ldots (10.30)$$

(*ii*) Differentiating eqn (10.29),

$$\left(\frac{d\bar{G}_i}{\partial P}\right)_T - \left(\frac{\partial \bar{G}_i^0}{\partial P}\right)_T = 0$$

or $$\bar{V}_i - \bar{V}_i^0 = 0\ ;\ \textit{i.e.},\ \bar{V}_i = \bar{V}_i^0$$

That is, the molal partial volume of a component in *ideal solutions* is the same as its molar volume in the pure state,

$$\therefore \triangle V_{\text{mix}} = 0 \qquad \ldots (10{\cdot}31)$$

(*iii*) From eqn (10.29), $$(\bar{G}_i/T) - (\bar{G}_i^0/T) = R \ln N_i$$

or $$\frac{\partial}{\partial T}(\bar{G}_i/T) - \frac{\partial}{\partial T}(\bar{G}_i^0/T) = 0,$$

or $$\frac{-\bar{H}_i}{T^2} + \frac{\bar{H}_i^0}{T^2} = 0, \qquad \text{(eqn. 6.26)}$$

or $$\bar{H}_i = \bar{H}_i^0$$

That is, in *ideal solutions*, the enthalpy of a component does not change. Hence, $\triangle H_{\text{mix}} = 0$ $\ldots$ (10.32) (*iv*) From eqn (10.29),

$$RT \ln N_i = \overline{G}_i - \overline{G}_i^0 = [\overline{H}_i - T\overline{S}_i] - [\overline{H}_i^0 - T\overline{S}_i^0]$$

$$= -T[\overline{S}_i - \overline{S}_i^0]$$

$$\therefore \quad \overline{S}_i - \overline{S}_i^0 = -R \ln N_i \qquad \ldots (10.33)$$

In *ideal solutions*, the entropy-increase of a component on going into solution is proportional to the logarithm of its mole-fraction.

Besides, the ideal solutions obey Raoult's Law which will be discussed soon.

10.9. Relation between fugacity and mole-fraction of components: Duhem-Margules Equation.

Suppose a binary solution contains n_1 gm-moles of A and n_2 gm-moles of B. Then, applying Gibbs-Duhem relation,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

or
$$\frac{n_1}{n_1 + n_2} d\mu_1 + \frac{n_2}{n_1 + n_2} d\mu_2 = 0$$

or
$$N_1 d\mu_1 + N_2 d\mu_2 = 0,$$

where N_1, N_2 are the mole-fractions, such that $N_1 + N_2 = 1$. Substituting the chemical potentials by expressions of fugacities given in equation (10.23),

$$N_1 RT\, d \ln \mathrm{f}_1 + N_2 RT\, d \ln \mathrm{f}_2 = 0$$

or
$$N_1 d \ln \mathrm{f}_1 + N_2 d \ln \mathrm{f}_2 = 0$$

or
$$N_1 \frac{d \ln \mathrm{f}_1}{dN_1} + N_2 \frac{d \ln \mathrm{f}_2}{dN_1} = 0$$

or
$$N_1 \frac{d \ln \mathrm{f}_1}{dN_1} - N_2 \frac{d \ln \mathrm{f}_2}{dN_2} = 0 \qquad [\because dN_1 = -dN_2]$$

or
$$\frac{d \ln \mathrm{f}_1}{d \ln N_1} = \frac{d \ln \mathrm{f}_2}{d \ln N_2} \qquad \ldots (10.34)$$

The same relation will hold true if the solution contains a large number of components, whose mole-fractions are N_1, N_2, N_3, N_4 etc., such that $N_1 + N_2 + N_3 + N_4 + \ldots = 1$.

Then $$dN_1 + dN_2 + dN_3 + dN_4 + \ldots = 0$$

or $$N_1\frac{dN_1}{N_1} + N_2\frac{dN_2}{N_2} + N_3\frac{dN_3}{N_3} + \ldots = 0$$

or $$N_1 d\ln N_1 + N_2 d\ln N_2 + N_3 d\ln N_3 + \ldots = 0.$$

or $$\lambda[N_1 d\ln N_1 + N_2 d\ln N_2 + N_3 d\ln N_3 + \ldots] = 0 \qquad \ldots (10.35)$$

From Gibbs-Duhem relations

$$N_1 d\mu_1 + N_2 d\mu_2 + N_3 d\mu_3 + \ldots = 0$$

or $$N_1 d\ln \mathrm{f}_1 + N_2 d\ln \mathrm{f}_2 + N_3 d\ln \mathrm{f}_3 + \ldots = 0 \qquad \ldots (10.36)$$

Equating the co-efficients in equations (10.35 and 10.36)

$$d\ln \mathrm{f}_1 = \lambda d\ln N_1, \quad d\ln \mathrm{f}_2 = \lambda d\ln N_2, \quad d\ln \mathrm{f}_3 = \lambda d\ln N_3$$

$$\ldots\ldots\ldots\ldots$$

or $$\frac{d\ln \mathrm{f}_1}{d\ln N_1} = \frac{d\ln \mathrm{f}_2}{d\ln N_2} = \frac{d\ln \mathrm{f}_3}{d\ln N_3} = \cdots = \frac{d\ln \mathrm{f}_i}{d\ln N_i} \cdots = \lambda \qquad \ldots (10.37)$$

This relation, commonly called the Duhem-Margules equation, is generally true. It is applicable to any liquid solution irrespective of whether the solution or the vapour is ideal or not.

In the case of ideal solutions, from equation (10.24)

$$\frac{d\ln \mathrm{f}_1}{d\ln N_1} = 1$$

and so all the ratios would tend to unity.

Further, when the vapours behave ideally, i.e., $\mathrm{f}_i = p_i$, (though the solutions may not be ideal), we have,

$$\frac{d\ln p_1}{d\ln N_1} = \frac{d\ln p_2}{d\ln N_2} = \frac{d\ln p_3}{d\ln N_3} = \cdots \qquad \ldots (10.38)$$

where p_1, p_2 etc. are the partial vapour pressures. This correlates the composition with the vapour-pressures. The physical significance of the relation will be realised when we would take up the study of the solutions.

10.10. The Dilute Solutions : Henry's Law

The characteristic properties of ideal solutions have just been discussed. For real and non-ideal solutions, there are considerable deviations in these properties. But the real solutions, in which the solute is present in very low concentrations ($Lt N_2 \rightarrow 0$), tend to behave like ideal solutions and are termed *dilute solutions*. The term solute refers to the component which is present in smaller proportion. Such dilute solutions have been found to obey some common laws, such as, Henry's Law, Raoult's Law etc. These laws are briefly mentioned here.

Henry's Law : It has been experimentally established that in dilute solutions, at a given temperature, the vapour pressure (P_2) of the solute is proportional to its concentration (c_2).

$$P_2 = kc_2\,;\quad (k \text{ is a constant}) \qquad \ldots (10.39)$$

This is *Henry's Law.*

Now, in idealised state the vapour pressure becomes equal to fugacity. In dilute solutions concentration c_2 is proportional to its mole-fraction, N_2 ; i.e., $c_2 = k'N_2$. Hence, Henry's law may be expressed as

$$\mathbf{f}_2 = P_2 = kk'N_2$$

$$\text{or} \qquad \mathbf{f}_2 = k_2 N_2 \qquad \ldots (10.40)$$

The value of the constant, k_2, depends upon the nature of the solvent and the solute and is different for different solutions.

In ideal solutions, $\mathbf{f}_2 = \mathbf{f}_2{}^{\theta} N_2$, (from eqn. 10.24) But equation (10.40) is applicable for real solutions and k_2 need not necessarily be equal to $\mathbf{f}_2{}^{\theta}$. In those cases, when $\mathbf{f}_2 - N_2$ curve remains linear throughout the entire range of concentration, k_2 will be equal to $\mathbf{f}_2{}^{\theta}$, the fugacity of the pure phase of the solute.

From eqn. (10.40), it is only found that the fugacity of the solute *in real dilute solutions* would be proportional to its mole-fraction. In very dilute solutions, equation (10.40) will always be valid. With increase in the value of N_2, deviations from the law are observed. With the acceptance of Henry's Law for dilute solutions, it is possible to deduce thermodynamically the other more important Raoult's Law for dilute solutions.

10.11. Raoult's Law

Let us consider a dilute binary solution containing N_2 mole-fraction of the solute with N_1 mole-fraction of the solvent. Their respective fugacities are denoted by $\mathbf{f}_2$ and $\mathbf{f}_1$.

From equation (10.40), the fugacity of the solute (Henry's Law),

$$\mathrm{f}_2 = k_2 N_2$$

$$\text{or} \quad d\ln \mathrm{f}_2 = d\ln N_2; \quad \text{i.e.,} \ \frac{d\ln \mathrm{f}_2}{d\ln N_2} = 1$$

From eqn (10.37),

$$\frac{d\ln \mathrm{f}_2}{d\ln N_2} = \frac{d\ln \mathrm{f}_1}{d\ln N_1}$$

Combining these,

$$\frac{d\ln \mathrm{f}_1}{d\ln N_1} = 1$$

or

$$d\ln \mathrm{f}_1 = d\ln N_1$$

i.e.,

$$\mathrm{f}_1 = k_1 N_1 \qquad \ldots (10.41)$$

where k_1 is a constant.

The equation (10.41) states that in the real dilute solutions, the fugacity of the solvent is also proportional to its mole-fraction. This is the basis of the Raoult's law.

This relation is valid in the range of composition where Henry's law holds true, i.e., when the solution is very dilute ($N_1 \rightarrow 1$), i.e. the pure solvent in the limit.

On the other hand, in an ideal solution, the fugacity of the solvent given as

$$\mathrm{f}_1 = \mathrm{f}_1^{\theta} N_1,$$

which is valid in the entire range of composition from $N_1 = 1$ to $N_1 = 0$. This equation then also represents the relation (10.41 for *infinitely dilute solutions*, *or* $k_1 = \mathrm{f}_1^{\theta}$.

If the vapour-phase of the solvent in equilibrium with the solution be regarded as ideal, the fugacities may be replaced by pressure ;

$$P_1 = P_1{}^0 N_1 \qquad \ldots (10.42)$$

where $P_1{}^0$ is the vapour-pressure of the pure solvent and P_1 is the partial vapour pressure of the solvent over the solution.

Since at a given temperature, $P_1{}^0$ is constant, we may state the Raoult's law as "*the vapour pressure of the solvent over the solution is proportional to its mole-fraction in the liquid solution.*"

In an *ideal* solution, the solvent follows Raoult's Law over entire range of composition. In an *ideal* solution, containing several volatile constituents, each of them would obey Raoult's Law.

$$p_i = N_i p_i^0 \qquad \ldots (10.43)$$

In other words, an ideal solution is one in which each component obeys Raoult's Law through the entire range of composition.

In real solutions, i.e., non-ideal solutions, considerable deviation from the Raoult's law is often observed, sometimes positive and sometimes negative.

If the solute be non-volatile, or when the solution is very dilute, the partial vapour pressure of the solute is negligible. So we may simply say, "*The vapour pressure of the solution is proportional to the mole-fraction of the solvent in the liquid phase.*"

10.11a. Nernst Distribution Law

We have just seen that the distribution of a component in a given system between the liquid and the gas phase is governed by the Raoult's Law and the Henry's Law. An interesting relation in the distribution of a solid (say) in two phases had been developed by Nernst.

It is known that the chemical potential of a component present in different phases of a system at eqm is the same in every phase. If a substance be present in two liquid phases, denoted by suffix I and II, at equilibrium, then (Sec. 10.2)

$$\mu_I = \mu_{II}$$

From (Sec. 10.12), $RT\ ln\ a_I + \mu_I^\circ = RT\ ln\ a_{II} + \mu_{II}^\circ$

Where a_I, a_{II} are the activities of the components in the two liquid phases. Then at const temperature, $a_I/a_{II} = K$ (constant) . . . (10.43*a*)

Thus, if the activity of a component in one phase be fixed, its activity in another phase at eqm is also fixed. In dilute solutions or ideal solutions, the activities may be replaced by concentrations C_1 and C_2. Then,

$$C_1/C_2 = K \qquad \ldots (10.43b)$$

where K is called the *Distribution coefficient or Partition coefficient* of the solute between the two solvents at the given temperature.

Consider a liquid-liquid system, say water and chloroform, to which a little quantity of iodine is added. Iodine will dissolve partly in water and partly in chloroform. The two solutions of iodine will separate into two layers at eqm. The concentrations in the two layers are different but their ratio is fixed, independent of the amount of iodine added or the volumes of the two liquids present.

The concentrations of a solute distributed between two phases at eqm at a constant temperature bear a fixed ratio. This is 'Nernst Distribution Law'.

The commonest use of this distribution principle is in the extraction of a solute by adding and shaking with immiscible solvents.

ACTIVITY

10.12. The activity

The function fugacity was introduced to express the molal free energy to cover the departures from ideal behaviour of the component. The determination of fugacity is linked up with gas pressure or vapour pressure. But often, the determination of fugacities become quite difficult as in the case of liquid mixtures or non-volatile substances.

Lewis, therefore, introduced another function called *activity* or *relative fugacity*, denoted universally by 'a'. If $\mathbf{f}$ and $\mathbf{f}^\circ$ denote the fugacities of a given substance in a given state and in a standard state, arbitrarily chosen, then the activity 'a' is the ratio of the two fugacities

$$a = \frac{\mathbf{f}}{\mathbf{f}^\circ} \quad \ldots (10.44)$$

It is obvious that, in that standard state, the activity

$$a^0 = \frac{\mathbf{f}^0}{\mathbf{f}^0} = 1$$

Also, $\overline{G} - \overline{G}^0 = RT \ln \frac{\mathbf{f}}{\mathbf{f}^0}$, or $\overline{G} - \overline{G}^0 = RT \ln a$ ... (10.45)

where $\overline{G}^\circ$ is the molal thermodynamic potential at the standard state. In a solution, for any component i, we shall have to take the partial molal quantities and hence

$$\overline{G}_i - \overline{G}_i^0 = RT \ln a_i \quad \ldots (10.46)$$

$$\left.\begin{array}{ll}\text{i.e.} & \mu_i - \mu_i^0 = RT \ln a_i \\ \text{or} & \mu_i = RT \ln a_i + \mu_i^0\end{array}\right\} \qquad \ldots (10.47)$$

Since the activity is a ratio of fugacities, its numerical value will depend upon the standard state which may be fixed at our convenience. This may be different in different cases.

10.13. The standard states

(*a*) **For Gases.** In gases and vapours, the standard state for the measurement of activity is taken as the one in which the fugacity is unity. Thus,

$$a = \frac{\mathbf{f}}{\mathbf{f}^0} = \frac{\mathbf{f}}{1} = \mathbf{f} \qquad \ldots (10.48)$$

i.e., the activity and the fugacity are numerically the same.

For a perfect gas, the fugacity and the pressure are equal, and the same is also true in case of other gases at low pressures.

Hence in such cases, $a = \mathbf{f} = P$

(*b*) **For pure liquids and solids.** The activities of liquids and solids in the pure state under 1 atmosphere pressure are taken as unity at each temperature. But when the liquid or the solid is present in a solution, it is not always convenient to assume the pure state as the standard for unit activity. It is necessary to consider the activities of solutes and solvents separately.

(*c*) **Solvents.** In the case of a solvent, the standard state is the pure state of the same at unit pressure. (As usual we shall use suffix 1 for solvent and 2 for solutes). That is, the pure solvent ($N_1 = 1$) is the standard state having unit activity ($a_1 = 1$), at each temperature.

If $\mathbf{f}_1{}^0$ is the fugacity in the pure state of the solvent, then, on addition of a solute, let the fugacity be $\mathbf{f}_1$. The activity a_1 of the solvent is

$$a_1 = \frac{\mathbf{f}_1}{\mathbf{f}_1{}^0}$$

In an ideal solution or in dilute real solution, Raoult's Law is applicable ; $\mathbf{f}_1 = \mathbf{f}_1{}^\circ N_1$. Hence, at unit pressure,

$$a_1 = \frac{\mathbf{f}_1{}^0 N_1}{\mathbf{f}_1{}^0} = N_1 \qquad \ldots (10.49)$$

That is, the activity of the solvent in a dilute real solution or in an ideal solution, at unit pressure, is equal to its mole-fraction. In a concentrated solution, where Raoult's Law is not obeyed, $\frac{a_1}{N_1}$ is different from unity and the values of the ratio at different concentrations will indicate the extent of departure from ideality. We shall later call this ratio as the *activity coefficient* (γ).

We should also remember that in any given solution, the activity of the solvent must be less than unity. If the activity were greater than unity, then the fugacity of the solvent in the solution would be greater than that in the pure state. So its escaping tendency from the solution would spontaneously separate it from the solution, which is against experience.

A consideration of the diagrams in Fig. 10*e* will bring out the significance of the standard state activities more clearly. In diagram I, vapour-pressures or fugacities are plotted against the mole-fraction of the solvent and in diagram II, the activities are plotted against the mole-fraction. (The vapours are supposed to behave ideally). In both the diagrams, the dotted line represents the behaviour of the ideal solution (Raoult's) and the solid line that of the real solution. The forms of the curves in the two diagrams shall be similar as fugacity is proportional to the activity.

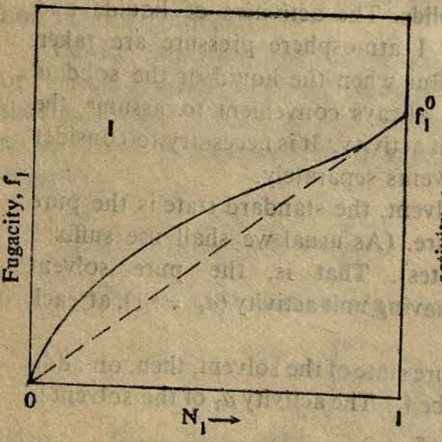

Fig. 10*e*. Fugacity and mol-fraction of the solvent

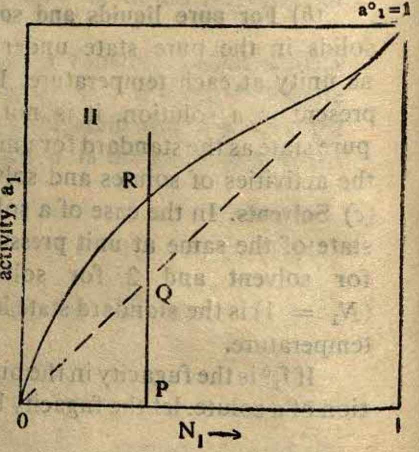

Fig. 10*e*. Activity and mol-fraction of the solvent

It is obvious that the dotted line in diagram II will have a slope of unity for when $N_1 = 1$, a_1 is equal to unity. This is not necessarily true in respect of the dotted line in diagram I. For a given soulution (diagram II), if PR denotes the activity of the solvent, PQ would denote the same under ideal behaviour. Hence, the ratio (activity coefficient),

$$\gamma = \frac{a_1}{N_1} = \frac{\text{PR}}{\text{OP}} = \frac{\text{PR}}{\text{PQ}}$$

Now, the activity of the solvent, $a_1 = \frac{\mathbf{f}_1}{\mathbf{f}_1^\circ} = \frac{p_1}{p_1^\circ}$ where p_1 and p_1° are the vapour-pressures of the solvent in the solution and in the pure state respectively, the vapours behaving perfectly. This gives us a useful method to calculate the activities.

To illustrate : An aqueous solution of an alcohol, in which the mole-fraction of the alcohol was 0.05, gave partial pressure of water and alcohol as 23.2 and 10.8 mm. respectively. The vapour-pressures in the pure state are $p = 21.76$ and $p_{\text{water}} = 23.8$ mm.

$$\text{The activity of the water, } a_1 = \frac{p_1}{p_1^0} = \frac{23.2}{23.8} = 0.98$$

$$\text{The activity of the alcohol, } a'_1 = \frac{p_1'}{p_1^{0\prime}} = \frac{10.8}{21.76} = 0.49$$

$$\text{The ratio (activity coefficient), } \gamma_{\text{water}} = \frac{a_1}{N_1} = \frac{0.98}{1-0.05} = 1.03$$

$$\gamma_{\text{alcohol}} = \frac{a_1'}{N_1'} = \frac{0.49}{0.05} = 9.8$$

(*d*) **Solutes.** In the case of solutions of solids or of electrolytes the standard state envisaged for the solute is somewhat different from that of the solvent. The standard state chosen for the solute may be either in terms of mole-fraction or in terms of molality.

(*i*) *On mole-fraction basis.* In dilute solutions, Henry's Law is obeyed, so the fugacity

$$\mathbf{f}_2 = k_2 N_2$$

If this relation be assumed to hold true through the entire range of composition until mole-fraction $N_2 \rightarrow 1$, (which is certainly hypothetical) then

$$Lt. N_2 \rightarrow 1 \; ; \; \mathbf{f}_2^\circ = k_2 . 1 = k_2$$

By definition, under these conditions, the activity of the solute,

$$a_2 = \frac{\mathbf{f}_2}{\mathbf{f}_2^\circ} = \frac{\mathbf{f}_2}{k_2}$$

and further, $$a_2 = \frac{f_2}{k_2} = \frac{k_2 N_2}{k_2} = N_2 \qquad \ldots (10.50)$$

The standard state selected for the solute is that hypothetical state of the solute, if its fugacity be supposed to obey the Henry's Law ($f_2 = k_2 N_2$), at a value of N_2 equal to unity, all at unit pressure. This is illustrated graphically in Fig. 10*f*.

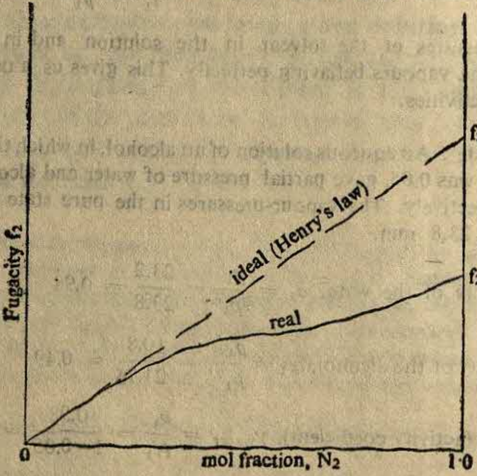

Fig. 10*f*. The standard state and fugacity of the solute

The curves in the Fig. 10*f* indicate the hypothetical nature of the assumption. The solid curve shows the actual fugacities of the solute through the entire range of composition up to $N_2 = 1$, when the fugacity is denoted by f_2^{θ}. This refers to the pure state of the solute. But in very dilute solutions, Henry's Law is obeyed. The dotted line shows the fugacities in the ideal state. At the lower values of N_2, the dotted line and the solid curve overlap each other. If this dotted line is extrapolated to $N_2 = 1$, we have the fugacity f_2° of the hypothetical state, which is the chosen standard state of the solute. It is evident,

$$f_2^{\circ} \neq f_2^{\theta}$$

The fugacity of the pure solute f_2^{θ} is quite different from the fugacity f_2° in the hypothetical state. Though the condition of the equation (10.50) is not realisable at high concentration, it would nevertheless hold true in very dilute solutions ($N_2 \rightarrow 0$).

It is thus possible to choose the infinitely dilute solution as the *reference state*, such that

$$Lt\, N_2 \to 0, \frac{a_2}{N_2} = 1$$

In the case of an ideal solution this will be valid through the entire range of composition. In real solutions, the validity is restricted to the dilute region only.

Now, in the hypothetical standard state, the activity,

$$a_2^0 = \frac{\mathbf{f}_2^0}{\mathbf{f}_2^0} = 1 \; ; (N_2 \to 1)$$

and further, the activity at any concentration in the hypothetical ideal solution is always given by,

$$a_2 = N_2.$$

So, if we plot the activity-mole-fraction curve for the ideal solution, then the slope of the curve shall be unity, as in Fig. 10*g*. The dotted line refers to the ideal solution and the solid line to the actual solution. The activity of the pure solute, a_2^θ (solid line, $N_2 \to 1$) is different from a_2°. At any composition N_i, the ratio $\frac{P'R'}{P'Q'}$ would denote the departure from the standard value.

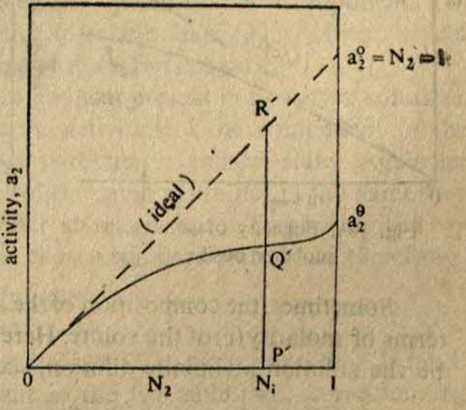

Fig. 10*g*. Activity and mol-fraction of the solute

(*ii*) *On molality basis* : The most common basis is to express the composition in terms of molality *m*, instead of mole-fraction *N*. The molality is defined as the number of gm-moles of the solute present in 1000 gm of the solvent. In very dilute solutions the molalities and mole-fractions are proportional. Hence, Henrys' Law ca be expressed as,

$$\mathbf{f}_2 = k'_2 m$$

The standard state of the solute, in this scale, should be the state which has the fugacity that the solute in one-molal solution would have if the solution obeyed the ideal solution Law (Henry's Law). This is shown in fig. 10*h*. As before, the reference state for the activity of the solute may be taken as the infinitely dilute solution such that

$$Lt.m \to 0, \quad \frac{a_2}{m} = 1.$$

So, by introducing the molal concentration we can change the curves of figure 10*h* into those of activity-molality as in Fig. 10*i*. The activity at the standard state ($m = 1$), in given by

$$a_2^0 = m = 1$$

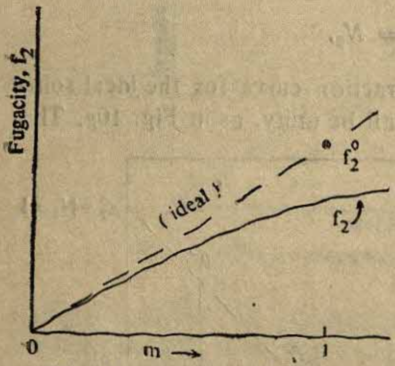

Fig. 10*h*. Fugacity of solutes in molality basis

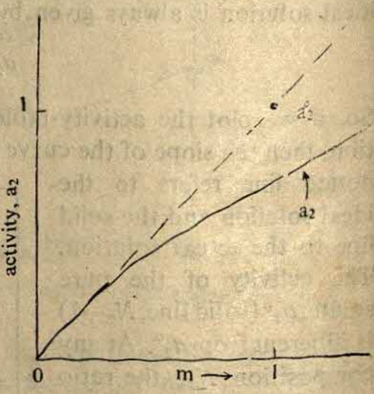

Fig. 10*i*. Activity of solutes in molality basis

Sometimes, the composition of the solution is also expressed in terms of molarity (c) of the solute. Here also, the refrence state may be the solution at infinite dilution, such that

$$Lt.c \to 0, \frac{a_2}{c} = 1.$$

The activity at the standard state state would be $a_2^0 = c = 1$

It should be understood that in every case, the unit pressure is to be maintained at constant temperature.

The deviation of $\frac{a_2}{N_2}$ $\left(\text{or } \frac{a_2}{m} \text{ or } \frac{a_2}{c}\right)$ from unity will obviously be a measure of the departure from ideality in the given solution.

10.14. The chemical potential and activity.

The chemical potential or the partial molal thermodynamic potential is expressed, by the equation (10.47)

$$\mu_i - \mu_i^0 = RT \ln a_i$$

Since μ_i^0 is constant a with a chosen reference state,

$$\mu_i = RT \ln a_i + Z_i \text{ constant}) \qquad \ldots (10.51)$$

Then in ideal systems and even in dilute real solutions, we have

$$\left.\begin{aligned} &\mu_i = RT \ln N_i + Z_{N_i} \\ \text{or} \quad &\mu_i = RT \ln m_i + Z_{m_i} \\ \text{or} \quad &\mu_i = RT \ln c_i + Z_{c_i} \end{aligned}\right\} \qquad \ldots (10.52)$$

in which the constants (z-terms) are the chemical potentials (μ_i^0) at the standard states.

Free-energy change and variation of standard of activity : The numerical value of the activity of a component in a solution depends naturally upon the reference state chosen for that component. But the change in thermodynamic quantities like $\triangle G$, $\triangle A$ etc. would be independent of the choice of the reference state.

Consider a particular component present in two given solutions x and y. Let a_x and a_y be the activities of the component in the two solutions, referred to a particular standard state. Again let a'_x and a'_y be the activities of the same substance in the same two solutions, referred to another standard state. These activities are relative to the activity in the chosen standard states, and therefore,

$$\frac{a_y}{a_x} = \frac{a'_y}{a'_x}$$

Now, let (μ_x and μ_y) and (μ'_x and μ'_y) represent the chemical potentials of the component in the two solutions, corresponding to two different standards. Then

$$\mu_x = RT \ln a_x + Z \qquad \mu_x' = RT \ln a'_x + Z'$$
$$\mu_y = RT \ln a_y + Z \qquad \mu_y' = RT \ln a'_y + Z'$$

$$\text{or,} \quad \mu_y - \mu_x = RT \ln \frac{a_y}{a_x} \quad \text{and} \quad \mu'_y - \mu'_x = RT \ln \frac{a'_y}{a'_x}$$

Since $a_y/a_x = a'_y/a'_x$, the change in chemical potentials i.e. the molal free-energy change would be the same and hence independent of the standard state chosen to compute the activities.

10.15. Variation of activity with temperature and with pressure.

We have,

$$d \ln a_i = d \ln \frac{\mathbf{f}_i}{\mathbf{f}_i^0}$$

or $$\left[\frac{\partial \ln a_i}{\partial P}\right]_{T,N} = \left[\frac{\partial \ln \mathbf{f}_i}{\partial P}\right]_{T,N} - \left[\frac{\partial \ln \mathbf{f}_i^0}{\partial P}\right]_{T,N}$$

Since $\mathbf{f}_1^0$ is a constant, the last term vanishes.

$$\left[\frac{\partial \ln a_i}{\partial P}\right]_{T,N} = \left[\frac{\partial \ln \mathbf{f}_i}{\partial P}\right]_{T,N} = \frac{\overline{V}_i}{RT}, \quad \text{(Sec. 10.7)} \ldots (10.53)$$

Similarly, $$\left[\frac{\partial \ln a_i}{\partial T}\right]_{P,N} = \left[\frac{\partial \ln \mathbf{f}_i}{\partial T}\right]_{P,N} - \left[\frac{\partial \ln \mathbf{f}_i^0}{\partial T}\right]_{P,N}$$

$$= \left[\frac{\partial \ln \mathbf{f}_i}{\partial T}\right]_{P,N} = \frac{\overline{H}_i^0 - \overline{H}_i}{RT^2} \quad \text{(Sec. 10.7)} \ldots (10.54)$$

These equations give the variations of the activity with pressure and temperature respectively.

10.16. Activity Coefficient

For many purposes, it is more convenient to use the ratio o the activity to the concentration than the real activity. This ratio of the activity to the concentration is termed the *activity coefficient*.

Three different units to express the composition of a solution, *viz*, mole-fraction N, molality m or molarity c are in use. As a result, there are three different expressions for the activity-coefficient of a component of the solution.

In infinitely dilute solution, $\frac{a_2}{N_2} = 1$, $\frac{a_2}{m} = 1$, $\frac{a_2}{c} = 1$

But as the concentration of the solute is increased, these relations are no longer valid and the ratios attain different values. (*a*) *The mole-fraction activity coefficient*, γ_N;

$$\gamma_N = \frac{a_2}{N_2}; \text{ or } a_2 = \gamma_N N_2 \quad \ldots (10.\ 5)$$

If it be a gas-mixture, then for any component i,

$$a_i = \frac{\mathbf{f}_i}{\mathbf{f}_i^\circ} = p_i \quad \text{(in an ideal case)}$$

In real systems, $a_i = \gamma_N p_i = \gamma_N N_i P$

where N_i = mol-fraction of the component, $p_i/P = N_i$

(*b*) *Molal activity coefficient* : For solutions of finite concentrations, the ratio will be the molal activity coefficient γ; when

$$\gamma = \frac{a_2}{m}; \text{ or } a_2 = \gamma m \qquad \ldots (10.56)$$

where m = molal concentration

(*c*) *Molar activity coefficient* : When the composition is expressed in molar units, the activity coefficient, f, will be given by

$$f = \frac{a_2}{c}; \text{ or } a_2 = fc \qquad \ldots (10.57)$$

where c is the concentration of the solute in molar units.

The activity coefficient γ_N, γ, and f obviously represent the deviations from the ideal state.

The chemical potentials for the component i in a solution may be obtained by introducing the activity coefficient in equation (10.51),

$$\mu_i = RT \ln a_i + Z_i$$

Then

$$\left.\begin{aligned} \mu_i &= RT \ln \gamma_{N_i} + RT \ln N_i + Z_{N_i} \\ \mu_i &= RT \ln \gamma_i + RT \ln m_i + Z_{m_i} \\ \mu_i &= RT \ln f_i + RT \ln c_i + Z_{c_i} \end{aligned}\right\} \qquad \ldots (10.58)$$

10.17. Activity coefficients of the solute in different units of the standard states.

Consider a solute present in two different solutions I and II. The solution I is an infinitely dilute one and the other solution II having a finite concentration, *c*. The acitivity of the solute in the infinitely dilute solution I is '$a°$' and that in solution II is 'a'. Then the change in chemical potential of the solute from solution I to solution II would be

$$\triangle\mu = \mu - \mu° = RT \ln \frac{a}{a°}$$

Expressing concentrations of the two solutions in three different units,

$$a = \gamma_N N; \quad a = \gamma m; \quad a = f.c$$

We have, $\frac{a}{a^\circ} = \frac{\gamma_N N}{N^\circ} = \frac{\gamma m}{m^\circ} = \frac{fc}{c^\circ}$ . . . (10.59)

the activity coefficients in infinite dilution being equal to unity.

The superscript° indicates ideal dilute solution.

We can determine the relation between the different activity coefficients if we know the relations between the concentration units.

Since m is the molality of the solution II, m moles of solute are dissolved in 1000 gm (or $1000/M_1$ mols) of the solvent.

Then, $$N = \frac{m}{m + 1000/M_1} = \frac{mM_1}{1000 + mM_1} \quad \ldots (10.60)$$

i.e., $$\frac{m}{N} = \frac{1000 + mM_1}{M_1} \quad \ldots (10.61)$$

Again c is the molarity of the solution *i.e.*, c gm-mols are dissolved in 1000 cc. of the solution.

1000 c.c. of the solution contains $\frac{1000\rho - cM_2}{M_1}$ gm-mols of the solvent.

Hence, $$N = \frac{c}{c + \frac{1000\rho - cM_2}{M_1}} = \frac{cM_1}{cM_1 - cM_2 + 1000\rho} \quad \ldots (10.62)$$

where ρ is the density of the solution (ρ_0 = density of pure solvent).

For solution I at infinite dilution m and c are negligibly small. Hence, equation (10.60 and 10.62) may be expressed as

$$N^\circ = \frac{m^\circ M_1}{1000} = \frac{c^\circ M_1}{1000\rho_0} \quad \ldots (10.63)$$

From equation (10.59),

$$\frac{\gamma_N}{\gamma} = \frac{m}{m^\circ} \cdot \frac{N^\circ}{N} = \frac{N^\circ}{m^\circ} \cdot \frac{m}{N}$$

Substituting from equation (10.61 and 10.63),

$$\frac{\gamma_N}{\gamma} = \frac{M_1}{1000} \times \frac{(1000 + mM_1)}{M_1} = 1 + 0.001\ mM_1 \quad \ldots (10.64)$$

Again from equation (10.59),

$$\frac{\gamma}{f} = \frac{c}{c^\circ} \cdot \frac{m^\circ}{m} = \frac{m^\circ}{c^\circ} \cdot \frac{c}{m}$$

Substituting from equation (10.60,62,63),

$$\frac{\gamma}{f} = \frac{1}{\rho_0} [\rho - 0.001\ cM_2] \quad \ldots (10{\cdot}65)$$

These equations provide the quantitative relations between the activity coefficients of the solute expressed in different concentration units.

10.18. Activities and Activity coefficients of Electrolytes

Solutions of electrolytes, especially of strong electrolytes, exhibit marked deviations from ideality even at low concentrations. As such the processes, in which ions are involved, must be recorded in terms of their activities. Only when the electrolyte solutions are at infinite dilution, the concentration terms could substitute the activities.

It is necessary to know how concentrations are converted to activities. Consider a solution of an electrolyte (A_xB_y) which is completely ionised in solution.

$$A_xB_y = x\mathrm{A}^{z+} + yB^{z-}$$

where z_+ and z_- are the charges of the ions. The subscripts + and − will always refer to properties of positive and negative ions ; symbols without subscript would refer to neutral molecules.

If there are c moles of the electrolyte dissolved in the c_s moles of solvent, then thermodynamic potential of the solution would be sum of the thermodynamic potentials of solvent and the ions, *i.e.*,

$$G = c_s\mu_s + c[x.\mu_+ + y\mu_-] \qquad \ldots (A)$$

μ-terms are the respective chemical potentials.

We also have $G = c_s\mu_s + c\mu \qquad \ldots (B)$

where μ is the chemical potential of the electrolyte in solution.

Comparing (A) and (B) $\mu = x\mu_+ + y\mu_- \qquad \ldots (C)$

Let $\nu = x+y$, the total number of ions produced from 1 molecule. And if $\mu_\pm$ is the mean ionic chemical potential, then

$$\nu.\mu_\pm = x\mu_+ + y\mu_- \qquad \ldots (D)$$

$$\therefore \qquad \mu = \nu\mu_\pm \qquad \ldots (E)$$

Now these chemical potentials may be expressed in the formal way,

$$\left.\begin{aligned} \mu_+ &= \mu_+^\circ + RT\,ln\,a_+ \\ \mu_- &= \mu_-^\circ + RT\,ln\,a_- \\ \mu_\pm &= \mu_\pm^\circ + RT\,ln\,a_\pm \\ \mu &= \mu^\circ + RT\,ln\,a \end{aligned}\right\} \qquad \ldots (F)$$

where a_+ and a_- are the activities of the ions, a is the activity of the electrolyte in solution, $a_{\pm}$ is the mean ionic activity. Moreover under standard states, by definition.

$$\mu^{\circ} = x\mu^{\circ}_{+} + y\mu^{\circ}_{-}$$

$$\nu\mu^{\circ}_{\pm} = x\mu^{\circ}_{+} + y\mu^{\circ}_{-}$$

i.e., $$\mu^{\circ} = \nu\mu^{\circ}_{\pm} \qquad \ldots (G)$$

Substituting (F) in (E), $\mu^{\circ} + RT\ ln\ a = \nu\mu^{\circ}_{\pm} + \nu RT\ ln\ a_{\pm}$

i.e., $$a = a_{\pm}^{\nu} \qquad \ldots (H)$$

Again, substituting equation (F) in (D),

$$\nu\mu^{\circ}_{\pm} + \nu\, RT\ ln\ a_{\pm} = x\mu^{\circ}_{+} + y\mu^{\circ}_{-} + x\, RT\ ln\ a_{+} + y\, RT\ ln a_{-}$$

i.e., $$a_{\pm}^{\nu} = a_{+}^{x} \,.\, a_{-}^{y} \qquad \ldots (I)$$

or $$a_{\pm} = \sqrt[\nu]{a} = \sqrt[\nu]{a_{+}^{x} \,.\, a_{-}^{y}} \qquad \ldots (J)$$

The mean ionic activity is the geometric mean of the individual ion activities.

Using formal expressions between activity and concentration,

$$\left.\begin{aligned} a &= fC \\ a_{\pm} &= f_{\pm}C_{\pm} \\ a_{+} &= f_{+}C_{+} \\ a_{-} &= f_{-}C_{-} \end{aligned}\right\} \qquad \ldots (K)$$

in which f-terms are the activity coefficients and C-terms are the concentrations in molar units.

Introducing equation (J)

$$a = a_{+}^{x}.a_{-}^{y} = (f_{+}C_{+})^{x}(f_{-}C_{-})^{y} = (C_{+}^{x} \,.\, C_{-}^{y}).f_{+}^{x}f_{-}^{y} \qquad \ldots (10.66)$$

and hence $$a_{\pm} = (C_{+}^{x} \,.\, C_{-}^{y})^{\frac{1}{\nu}} \,.\, (f_{+}^{x}f_{-}^{y})^{\frac{1}{\nu}} \qquad \ldots (10.67)$$

Aided by relations in (H),

mean activity coefficient of the electrolyte, $f_{\pm} = (f_{+}^{x} \,.\, f_{-}^{y})^{\frac{1}{\nu}}$

and *mean molarity of the electrolyte*, $C_{\pm} = (C_{+}^{x}.\, C_{-}^{y})^{\frac{1}{\nu}}$

$$\left.\begin{aligned} &\text{Thus,} & a_{\pm} &= a^{\frac{1}{\nu}} = C_{\pm} \cdot f_{\pm} \\ &\text{and} & a &= a_{\pm}^{\nu} = (C_{\pm}.f_{\pm})^{\nu} \end{aligned}\right\} \qquad \ldots (10.68)$$

If we consider a solution of molarity C, then

$$C_+ = xC; \quad C_- = yC$$

So $$a_\pm = \sqrt[\nu]{a} = [(xC)^x (yC)^y]^{\frac{1}{\nu}} f_\pm$$

$$\left.\begin{aligned} &= (x^x y^y)^{\frac{1}{\nu}}\, C.f_\pm \\ \text{and} \quad a &= (x^x y^y) C^\nu f_\pm^\nu \end{aligned}\right\} \quad \ldots (10.69)$$

These expressions correlates concentration and activity.

For a uni-univalent type of electrolyte,

$$x = 1,\ y = 1,\ x + y = \nu = 2,$$

hence $$a_\pm = (1 \times 1)^{\frac{1}{2}}.\ C.\ f_\pm = C \cdot f_\pm$$

and $$a = a_\pm^2 = C^2 f_\pm^2$$

For a uni-bivalent type (say $BaCl_2$), $x = 1,\ y = 2,\ \nu = 3$,

hence $$a_\pm = (1 \times 2^2)^{\frac{1}{3}} C.\ f_\pm, = \sqrt[3]{4}.C.f_\pm$$

and $$a = a_\pm^3 = 4C^3 f_\pm^3$$

For some simple electrolytes, the expression for $a_\pm$ and a are given below :

TABLE: EXPRESSIONS FOR $a_\pm$ AND a FOR DIFFERENT ELECTROLYTES

Electrolyte	*type*	x, y	ν	$C_\pm$	$a_\pm$	$(a = a_\pm^\nu)$
$NaCl$, $ZnSO_4$ etc.	1−1	1, 1	2	C	$Cf_\pm$	$C^2 f_\pm^2$
$CaCl_2$, Na_2SO_4 etc.	1−2 or 2−1	1, 2	3	$\sqrt[3]{4}.C$	$\sqrt[3]{4}\, Cf_\pm$	$4C^3 f_\pm^3$
$La(NO_3)_3$, K_3PO_4 etc.	1−3 or 3−1	1, 3	4	$\sqrt[4]{27}.C$	$\sqrt[4]{27}\, Cf_\pm$	$27C^4 f_\pm^4$

When concentrations are given in molal units (m), the same procedure will give

$$a_+ = \gamma_+ m_+, \quad a_- = \gamma_- m_-\ , \quad a_\pm = (x^x y^y)^{\frac{1}{\nu}}\, m.\gamma_\pm$$

and $$a = a_\pm^\nu = (x^x y^y) m^\nu\, (\gamma_\pm)^\nu$$

γ-terms are their activity coefficients and m-terms molal concentrations.

Also, $$\gamma_\pm = (\gamma_+{}^x \cdot \gamma_-{}^y)^{1/\nu}$$

10-19. Ionic Strength

It is necessary to define another term namely, *the ionic-strength* which will have to be frequently used in our subsequent discussions.

Experimental observations showed that the activity coefficient of a given strong electrolyte in very dilute solutions begins to decrease with rise in concentration, reaches a minimum and then increases with concentration. The curves shown in Fig. 10*j* illustrate this fact. It was soon realised that in very dilute solutions, *the activity coefficients of electrolytes of the same type (say, uni-univalent or bi-bivalent types) are practically the same at the same ion concentration.* The table below will bear out the truth of this statement.

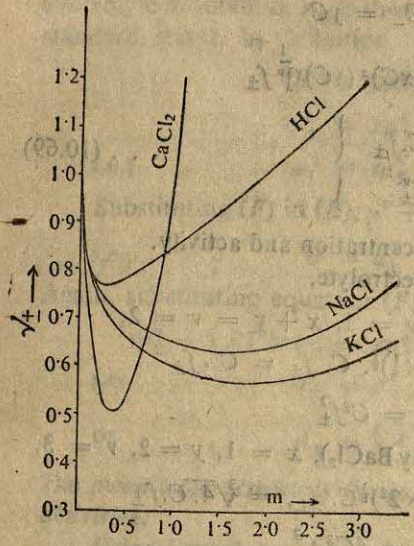

Fig. 10*j*. Activity coefficients of electrolytes at various concentrations

TABLE : ACTIVITY COEFFICIENTS OF STRONG ELECTROLYTES

Conc. (m)	1×10^{-3}	5×10^{-3}	1×10^{-2}
HCl	0.966	0.928	0.905
NaCl	0.966	0.929	0.904
KCl	0.965	0.927	0.901
KBr	0.965	0.927	0.903
KI	0.965	0.927	0.905
NaBr	0.966	0.934	0.914
CaCl$_2$	0.888	0.789	0.731
ZnCl$_2$	0.880	0.789	0.731

Empirically the mean activity coefficient may be represented as,

$$\ln \gamma_\pm = -A_1\sqrt{c}$$

where c is the concentration of the solute and it is valid at extremely low concentrations.

In a mixture, the activity coefficient of a given electrolyte depends upon the total electrolyte concentration as also on the individual characters of the different ions present. When a mixture contains salts of the same ion type (say all bi-bivalent) the activity coefficient of a given electrolyte in very dilute solutions is the same in all solutions of the same total normality. In more concentrated solutions, the specific character of the ions influences the activity coefficient.

Lewis and Randall found that the influence of an ion in a mixture on the activity coefficient of a given electrolyte is proportional to the square of its valency. That is, a bivalent ion (say Ba^{++}) influences the activity coefficient of a salt (say $NaNO_3$) in a mixture four times a K^+ ion. For the purpose of comparing the activity coefficients of electrolytes in the pure state as also in the mixtures with other electrolytes, Lewis and Randall introduced a quantity called the *ionic strength*, denoted by i. This is obtained by multiplying the molality of each ion present in the solution with the square of its valency and dividing the sum of these products by two. Suppose a solution contains different ions having molalities $m_1, m_2, m_3 \ldots$ with valencies, $z_1, z_2, z_3 \ldots$ etc. The ionic strength of the solution would be

$$i = \tfrac{1}{2}[m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \ldots] = \tfrac{1}{2} \Sigma mz^2$$

In a sense, the ionic strength is a measure of the effective influence of all the ions in the solution.

Lewis and Randall further stated that in very dilute solutions, *the activity coefficient of an electrolyte is the same in all solutions of the same ionic strength.* This rule holds strictly in very dilute solutions, say up to $i = 0.01$.

The ionic strength of solutions of pure salts (molality, m) are shown below :

Electrolyte	Molality	Valency	i, ionic strcngth
(*i*) Uni-univalent, ($NaNO_3$)	$m_{Na+} = m$	$Z_{Na+} = 1$	$i = \frac{1}{2}(m.1^2 + m.1^2)$
	$m_{NO_3-} = m$	$Z_{NO_3-} = 1$	$= m$
(*ii*) Uni-bivalent, ($CaCl_2$)	$m_{Ca++} = m$	$Z_{Ca++} = 2$	$i = \frac{1}{2}(m.2^2 + 2m.1^2)$
	$m_{Cl-} = 2m$	$Z_{C-} = 1$	$= 3m$
(*iii*) Bi-bivalent, ($MgSO_4$)	$m_{Mg++} = m$	$Z_{Mg++} = 2$	$i = \frac{1}{2}(m.2^2 + m.2^2)$
	$m_{SO_4--} = m$	$Z_{SO_4--} = 2$	$= 4m$
(*iv*) Uni-trivalent, ($LaCl_3$)	$m_{La+++} = m$	$Z_{La+++} = 3$	$i = \frac{1}{2}(m.3^2 + 3m.1^2)$
	$m_{Cl-} = 3m$	$Z_{Cl-} = 1$	$= 6m$

Similarly, a solution containing 0.008m $BaCl_2$ and 0.005 m KCl will have its ionicstrength, calculated as follows :

$$m_{Ba^{++}} = 0.008 \; ; \; m_{Cl^-} = 2\times0.008+0.005 = 0.021 \; ; \; m_{K^+} = 0.005$$

$$\therefore \; i = \tfrac{1}{2}[0.008\times2^2 + 0.005\times1^2 + 0.021\times1^2] = 0.029$$

Methods which are commonly used for the determination of activity and activity coefficients will be dealt with in a subsequent chapter.

Problems

1. The van der Waals constants for CO_2 gas are $a = 3.59\times10^6$ cc²-atm/mole², and $b = 42.7$ cc./mole. Show that the fugacity of the gas at 100 atm. pressure and 50°C is approximately 64 atmospheres.

2. Show that, for a Berthelot gas, at a pressure P and temperature T.

$$ln\,(f/p) = AP, \text{ where } A = \frac{9}{128}\cdot\frac{T_c}{TP_c}\left(1-6\,\frac{T_c^2}{T^2}\right), \text{ f is the fugacity of the gas.}$$

3. At 37°C, in a gas mixture methane is present in a concentration of 0.17 mol-fraction. Its critical constants are $T_c = 190.5$°K and $P_c = 45.8$ atm. What will be its fugacity when the total pressure is 20.4 atmospheres. Ans. 3.4 atm.

4. Assuming carbon dioxide as a Berthelot gas, calculate its fugacity at 423°K and 50 atmospheres. Given $T_c = 304$°K and $P_c = 50$ atm.
Ans. 46 atm.

5. If P be the total vapour pressure over a binary liquid mixture (1 and 2), show that

$$\frac{dp}{dN_1} = \frac{dp_2}{dN_2}\left(\frac{N_2p_1}{N_1p_2} - 1\right), \text{ vapours behaving ideally.}$$

CHAPTER 11

STATISTICAL CONSIDERATIONS

11.1. Introduction

In chapter 5, it has been shown that the entropy of a system at equilibrium can be evaluated sufficiently accurately from the most probable macrostate, which has the largest number of microstates. The thermodynamic probability is then expressed in terms of n_i-values for the most probable macrostate, and $S = k \ln W$.

In a system containing a collection of particles or molecules, each can be in any of the various available energy levels and spatial distributions. The macroscopic properties of the system depend on how many molecules are occupying the different states. It has now been possible to develop statistical methods to obtain information of the distribution of molecules among the possible states. This enables one to evaluate the various properties of the bulk system. In fact, there are now three different equations for (W) the thermodynamic probability which are required to meet different physical systems. The three statistics, as they are called, are those of (*i*) Maxwell-Boltzmann (M-B), (*ii*) Bose-Einstein (B-E), (*iii*) Fermi-Dirac (F-D). The M-B statistics were introduced in the latter part of the last century, when rules of quantisation of energy were not known. Further in the M-B statistics it was assumed that the particles are independent but distinguishable. This statistics was therefore quite suitable in dealing with solid systems where particles have distinct positions in the crystal lattice. But for gases where identical indistinguishable particles are concerned, this statistics would be unsatisfactory. It has to be appropriately modified in its application to gases.

The other two statistics — the 'quantum' statistics of Bose-Einstein and Fermi-Dirac — can be applied to systems containing identical indistinguishable particles. The Fermi-Dirac statistics is applied to systems in which the particles (like nuclei, atoms, molecules) contain an odd number of elementary particles of electron, proton and neutron. This it is suitable for systems of D (deuterium), NO, NH_3, ^3He etc. The Bose-Einstein statistics is applied to systems of particles having even number of elementary particles, such as systems of atomic H, H_2, N_2, ^{4}He, etc. The degeneracy of each quantum level with a very large number of states is accepted in both these statistics. The shifting of a particle from one state to another in the same level leads to a new arrangement. Further in F-D statistics, only one particle is allowed in any energy state but in B-E statistics (as well as in M-B statistics) there is no restriction in the number of particles to be accommodated in anyenergy state.

The particles which obey the M-B statistics have now been named '*Boltzons*', where as the particles following B-E and F-D statistics are called now '*bosons*' and '*fermions*' respectively. We shall shart with the Maxwell-Boltzmann distribution first.

11.2. The Boltzmann Distribution Law

Consider a system containing n molecules having a total energy E; n of course is very large. The particles are not in the same energy-level. Let there be a given distribution, n_0 molecules in energy-level ϵ_0, n_1 in energy level ϵ_1, n_2 in energy-level ϵ_2 and so on.

Then, we have,

$$E = n_0\epsilon_0 + n_1\epsilon_1 + n_2\epsilon_2 + \ldots + n_i\epsilon_i + \ldots = \Sigma n_i\epsilon_i \quad \ldots (11.1)$$

and also,

$$n = n_0 + n_1 + n_2 + \ldots n_i + \ldots = \Sigma n_i \quad \ldots (11.2)$$

The thermodynamic probability of a given distribution (eqn. 5.24),

$$W = \frac{n\,!}{n_0\,!\,n_1\,!\,n_2\,!\ldots n_i\,!\ldots} = \frac{n\,!}{\Pi\, n_i\,!}$$

Hence $\quad ln\ W = ln\ n\,! - \Sigma\, ln\ n_i$

Since n as also n_i are very large, we can apply Stirling's theorem,

$$ln\ x\,! = x\ ln\ x - x$$

Therefore, $\quad ln\ W = (n\ ln\ n - n) - (\Sigma n_i\ ln\ n_i - \Sigma n_i)$

As $n = \Sigma n_i$, $\quad ln\ W = n\ ln\ n - \Sigma n_i\ ln\ n_i \quad \ldots (11.3)$

Now, as the occupation numbers $n_1, n_2, n_3 \ldots$ etc. in different energy levels change, the thermodynamic probability changes. It will be maximum when the distribution corresponding to the equilibrium is attained. That is at eqm. distribution, the magnitude of

W, and hence of $ln\ W$, will be maximum. Therefore, at equilibrium, $d\ ln\ W = 0$. From eqn. (11.3) at eqm.,

$$d\ ln\ W = d(n\ ln\ n) - d(\Sigma n_i\ ln\ n_i) = 0$$

As n is constant, $\quad d(\Sigma n_i\ ln\ n_i) = 0$

or $\quad \Sigma\ ln\ n_i\, dn_i + \Sigma dn_i = 0$

But $\Sigma n_i = n$ (constant), $\quad \therefore\ \Sigma dn_i = 0$

$$\therefore\ \Sigma\ ln\ n_i\ dn_i = 0 \qquad \ldots (11.4)$$

We must remember that for the given system the total energy E and the total number of particles n remain constant, *i.e.*

$$n = \Sigma\, n_i; \quad \text{or} \quad dn = \Sigma\, dn_i = 0 \qquad \ldots (11.5)$$

$$E = \Sigma\, n_i \epsilon_i \quad \text{or} \quad dE = \Sigma\, \epsilon_i dn_i = 0 \qquad \ldots (11.6)$$

Multiplying these equations by undetermined arbitrary multipliers α and β respectively and adding equation (11.4), we have

$$\Sigma\ ln\ n_i\, dn_i + \alpha\ \Sigma dn_i + \beta \Sigma \epsilon_i dn_i = 0$$

or $\quad [\Sigma\ ln\ n_i + \alpha + \beta \Sigma \epsilon_i]\ dn_i = 0$

Since α and β are independent, the restraining conditions are removed, and $dn_i \neq 0$, this relation will be true for any energy-level or cell ; hence

$$ln\, n_i + \alpha + \beta \epsilon_i = 0$$

or $\quad n_i = e^{-\alpha}\, e^{-\beta \epsilon_i} \qquad \ldots (11.7)$

This is the expression for the number of particles in each energy-level, α, β being unknown arbitrary constants.

$$n = \Sigma\, n_i = e^{-\alpha} \Sigma e^{-\beta \epsilon_i} \qquad \ldots (11.8)$$

or $\quad n_i = \dfrac{n.e^{-\beta \epsilon_i}}{\Sigma e^{-\beta \epsilon_i}} \qquad \ldots (11.9)$

This is known as the *Boltzmann Distribution Law.* It gives at a temperature T the fraction of total number of molecules which at eqm. or most probable state would possess energy ϵ_i.

The expressions in equations 11.8 and 11.9 have to be modified as the energy-levels are largely degenerate. In such cases, the thermodynamic probability W is given by equation (5.27),

$$W = \Pi\, \frac{(g_i)^{n_i}}{n_i\,!}$$

Proceeding as before, when at eqm. W becomes maximum,

$$ln\, W = \Sigma(n_i\, ln\, g_i - n_i\, ln\, n_i + n_i)$$

$$= \Sigma\left(n_i\, ln \frac{g_i}{n_i}\right) + n$$

or $$d\, ln\, W = \Sigma\, ln\, \frac{g_i}{n_i}\, dn_i = 0$$

With the help of eqns (11.5, 11.6) and using undetermined multipliers α and β as before,

$$[\Sigma\, ln\, (g_i/n_i) dn_i + \alpha\Sigma dn_i + \beta\, \Sigma\epsilon_i dn_i] = 0$$

or $$[\Sigma\, ln\, (g_i/n_i) + \alpha + \beta\Sigma\epsilon_i]\, dn_i = 0$$

Since α, β are arbitrary constants, and $dn_i \neq 0$, hence for any energy-level,

$$ln\, (g_i/n_i) + \alpha + \beta\epsilon_i = 0$$

or $$n_i = g_i e^{-\alpha} e^{-\beta\epsilon_i} \qquad \ldots (11.10)$$

and $$n = \Sigma n_i = e^{-\alpha}\Sigma g_i e^{-\beta_i} \qquad \ldots (11.11)$$

$\therefore$ $$n_i = \frac{n\, g_i e^{-\beta\epsilon_i}}{\Sigma g_i\, e^{-\beta\epsilon_i}} \qquad \ldots (11.12)$$

Putting $A = \frac{1}{n}\, \Sigma g_i\, e^{-\beta\epsilon_i}$, the eqn (11.12) is sometimes written as

$$n_i = \frac{g_i}{A.e^{\beta\epsilon_i}} \qquad \ldots (11.13)$$

11.3. The Partition Function

The denominator $\Sigma e^{-\beta\epsilon_i}$ in the expression of the equation 11.9 is the sum of the factor $e^{-\beta\epsilon_i}$ over all the energy-levels. It is called the *molecular partition function* or *zustandssumme* and may be denoted by f.

$$f = \Sigma e^{-\beta\epsilon_i} \qquad \ldots (11.14)$$

where β is called the modulus of distribution.
The Boltzmann distribution may then be expressed as

$$n_i = \frac{n}{f}\, e^{-\beta\epsilon_i} \qquad \ldots (11.15)$$

or $$ln\, n_i = ln\, n - ln\, f - \beta\epsilon_i \qquad \ldots (11.16)$$

It should be noted that the partition function is a dimensionless number. Its importance lies in the fact that it is essentially required in the statistical evaluation of different properties of particles in a system. In other words, it would be demonstrated that various macroscopic properties of a system may be expressed in terms of f.

Evaluation of β. At equilibrium when W attains maximum value, the entropy (S) is given by

$$S = k \ln W$$

or

$$S/k = n \ln n - \Sigma n_i \ln n_i \quad \text{(from eqn 11.3)}$$

$$= n \ln n - \Sigma n_i (\ln n - \ln f - \beta \epsilon_i) \quad \text{(from eqn11.16)}$$

$$= n \ln n - \ln n \,.\, \Sigma n_i + \ln f \,.\, \Sigma n_i + \beta \, \Sigma n_i \epsilon_i$$

$$= n \ln n - n \ln n + n \ln f + \beta E, \quad (\text{since } E = \Sigma n_i \epsilon_i)$$

or

$$S = n k \ln f + k \beta E \qquad \ldots (11.17)$$

Differentiating,

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{nk}{f}\left(\frac{\partial f}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial E}\right)_V + k\beta + kE\left(\frac{\partial \beta}{\partial E}\right)_V$$

But $f = \Sigma e^{-\beta \epsilon_i}$; $\therefore$ $\left(\frac{\partial f}{\partial \beta}\right)_V = - \Sigma \epsilon_i e^{-\beta \epsilon_i}$

$$= - \Sigma \epsilon_i \frac{n_i}{e^{-\alpha}} \quad \text{(from eqn 11.7)}$$

$$= - \Sigma \epsilon_i \frac{n_i}{n/f} \quad \text{(from eqn 11.8)}$$

$$= - \frac{E}{n} f \qquad \ldots (11.18)$$

Substituting,

$$\left(\frac{\partial S}{\partial E}\right)_V = -\frac{nk}{f} \cdot \frac{E}{n} f \left(\frac{\partial \beta}{\partial E}\right)_V + k\beta + kE\left(\frac{\partial \beta}{\partial E}\right)_V$$

or,

$$\left(\frac{\partial S}{\partial E}\right)_V = k\beta$$

When the energy is purely the internal energy, *i.e.*, $E = U$, then

$$\left(\frac{\partial S}{\partial U}\right)_V = k\beta$$

But, from the First and Second Laws, $dU + pdv = dQ = TdS$,

or $$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

Hence $$k\beta = \frac{1}{T}, \text{ or } \beta = \frac{1}{kT} \quad \ldots (11.19)$$

$$\therefore \text{ the partition function, } f = \Sigma e^{-\frac{\epsilon_i}{kT}} \quad \ldots (11.20)$$

and $$n_i = \frac{n}{f} e^{-\frac{\epsilon_i}{kT}} \quad \ldots (11.21)$$

Substituting β in eqn 11.7, the number of molecules, each having energy ϵ_i at temp. T, is

$$n_i = e^{-\alpha} e^{-\beta\epsilon_i} = e^{-\alpha} e^{-\epsilon_i/kT} = \text{constant. } e^{-\epsilon_i/kT} \quad \ldots (11.22)$$

Hence, "*In a system at equilibrium, the number of molecules possessing energy, ϵ_i each, is proportional to the Boltzmann factor, $e^{-\epsilon_i/kT}$*.

If the degeneracy of the states are considered, we would have,

$$\left.\begin{aligned} f &= \Sigma g_i e^{-\frac{\epsilon_i}{kT}} \\ n_i &= \frac{n}{f} \cdot g_i e^{-\frac{\epsilon_i}{kT}} \end{aligned}\right\} \quad \ldots (11.23)$$

Qualitatively speaking, the partition function indicates how the particles are distributed among the various energy states. It is a measure of available energy-levels.

From eqn (11.13), $$A = \frac{f}{n} = \frac{\text{sum over states}}{\text{sum over particles}} \quad \ldots (11.24)$$

11.4. Applicability of M-B Statistics

Re-writing equation 11.23, we have

$$\frac{g_i}{n_i} = \frac{f}{n} e^{\beta\epsilon_i} \quad \ldots (11.25)$$

At the ground state, $\epsilon_i = 0$, $\dfrac{g_0}{n_0} = \dfrac{f}{n}$

At any other level, since $e^{\beta\epsilon_i} > 1$, hence g_i/n_i is always greater than g_0/n_0.

$$\text{Hence} \quad \frac{g_0}{n_0} < \frac{g_1}{n_1} < \frac{g_2}{n_2} < \frac{g_3}{n_3} < \ldots < \frac{g_i}{n_i} \ldots$$

That is, the higher the energy-level the larger would be the value of the *dilution ratio* g_i/n_i; *i.e.* more quatum states would be available for each particle. If g_0/n_0 is large enough at the ground state, the particles are likely to be distributed as one in each state like the fermions. In such a widely dispersed state or highly dilute system, *M-B* statistics would be quite statisfactory even for perfect gases.

To illustrate, let us take, for simplicity, an ideal monatomic gas like helium or neon and find out the f/n-value. For monatomic gases, translational energy only is to be considered as vibration and rotation are absent. The partition function for translational energy, anticipated from section. 11.9, is given by,

$$f = \frac{(2\pi mkT)^{3/2}}{h^3} . V$$

or

$$\frac{f}{n} = \frac{(2\pi mkT)^{3/2}}{h^3} . \frac{V}{n} \;;\; (n \text{ molecules being present in } V \text{c.c.})$$

$$= \frac{(2\pi MRT)^{3/2}}{N^3 h^3} . \frac{82T}{N.P} \;;\; (P \text{ in atmospheres, } N\text{, avogadro number})$$

Putting the values of R, N and h,

$$\frac{f}{n} = 0.026 \ M^{3/2}\, T^{5/2}/P \qquad \ldots (11.26)$$

At 1 atm pressure and 27°C,

$$\text{for helium, } \frac{f}{n} = 3.2 \times 10^5$$

$$\text{and} \quad \text{for neon, } \frac{f}{n} = 3.5 \times 10^6$$

In these conditions, the dilution ratio is very large and *M-B* statistics will be applicable in both the cases.

An attempt may now be made to find out the dilution ratio for the *electron gas* in metals. Metals are now regarded to be constituted of the nuclei of atoms arranged in a stationary lattice and the electrons freely move around behaving like gases, which is termed 'electron-gas' of metals. Sodium crystallises in a cubic lattice. From X-ray measurements, it is found that the available volume per electron in sodium lattice is 4×10^{-23} cc.

$$\text{Hence}\qquad \frac{f}{n}=\frac{(2\pi kTm)^{3/2}}{h^3},\cdot\frac{V}{n}$$

$$=\frac{(2\pi kTm)^{3/2}}{h^3}\times 4\times10^{-23}$$

$$=4.8\times10^{-4}$$

But this is absurd, since f/n can never be less than unity. In other words, *M-B* statistics will not hold for an electron-gas. It may be argued that the f/n-value may be increased by raising the temperature T. It will be easily seen that to have a dilution of 10, *i.e.* $f/n=10$, the temperature for *solid* sodium should be 200000°K, which is impossible. In fact, electron-gas is governed by Fermi-Dirac statistics.

Again, from equation 11.26, it is obvious that with increase in temperature or decrease in pressure, f/n would increase, hence the energy-level spacings would be closer.

11.5. Partition function and thermodynamic quantities

It is easy to express and evaluate the different thermodynamic functions with the help of partition functions.

(*i*) **Internal Energy, U.** The internal energy (U) of a system of n molecules (in excess of that at the absolute zero) is

$$U=\Sigma\epsilon_i n_i=\Sigma\epsilon_i\left(\frac{n}{f}\cdot e^{-\frac{\epsilon_i}{kT}}\right).$$

$$\text{or}\qquad U=\frac{n}{f}\Sigma\epsilon_i e^{-\frac{\epsilon_i}{kT}}$$

$$\text{But}\qquad f=\Sigma e^{-\frac{\epsilon_i}{kT}},\quad\text{hence}\quad\frac{df}{dT}=\frac{1}{kT^2}\Sigma\epsilon_i e^{-\frac{\epsilon_i}{kT}}$$

$$\text{or}\qquad \Sigma\epsilon_i e^{-\frac{\epsilon_i}{kT}}=kT^2\frac{df}{dT}$$

Substituting, the internal energy

$$U=\frac{n}{f}\Sigma\epsilon_i e^{-\frac{\epsilon_i}{kT}}=\frac{nkT^2}{f}\frac{df}{dT}=nkT^2\frac{d\ln f}{dT}\qquad\ldots(11.27)$$

For a gm-mole, $U = N_0 kT^2 \dfrac{d\, ln f}{dT}$,

where N_0 = Avogardo number.

The average energy of each molecule, $\bar{\epsilon} = kT^2 \dfrac{d\, ln f}{dT}$ ... (11.28)

(*ii*) **Entropy, S.** From eqn. (11.17),

$$S = nk\, ln f + k\beta U$$

Since $\beta = \dfrac{1}{kT}$, we have $S = nk\, ln f + \dfrac{U}{T}$ ... (11.29)

Subsituting U by equation (11.27),

$$S = nk\, ln f + nkT \frac{d\, ln f}{dT} \quad \text{... (11.30)}$$

(*iii*) **Work Function, A.** We know $A = U - TS$

Using U and S in terms of partition function f, as expressed above,

$$A = U - T\left[nk\, ln f + \frac{U}{T} \right]$$

or $$A = -nkT\, ln f \quad \text{... (11.31)}$$

(*iv*) **Pressure, P.** Since $dA = -PdV - SdT$

or $$P = -\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial A}{\partial f}\right)_T \left(\frac{\partial f}{\partial V}\right)_T$$

Since $A = -nkT\, ln f$, $\left(\dfrac{\partial A}{\partial f}\right)_T = -\dfrac{nkT}{f}$

$$\therefore \quad P = \frac{nkT}{f}\left(\frac{\partial f}{\partial V}\right)_T = nkT\left(\frac{\partial\, ln f}{\partial V}\right)_T \quad \text{... (11.32)}$$

(*v*) **Gibb's Potential, G.** Since $G = A + PV$, we can write

$$G = -nkT\, ln f + nkT\left(\frac{\partial\, ln f}{\partial V}\right)_T V$$

or $$G = -nkT\left[ln f - \left(\frac{\partial\, ln f}{\partial\, ln V}\right)_T \right] \quad \text{... (11.33)}$$

(*vi*) **Heat Content, H.** The heat content, $H = U + PV$. Substituting with equations (11.25 and 11.26),

$$H = nkT^2 \frac{d \ln f}{dT} + nkT \left(\frac{\partial \ln f}{\partial V}\right)_T V$$

or $$H = nkT \left[\left(\frac{d \ln f}{d \ln T}\right) + \left(\frac{\partial \ln f}{\partial \ln V}\right)_T\right] \quad \ldots (11.34)$$

(*vii*) **Heat Capacity, C_V.** By definition, $C_V = \left(\frac{dU}{dT}\right)_V$

Hence $$C_V = nk \frac{d}{dT}\left(\frac{T^2 \partial \ln f}{\partial T}\right)_V \quad \ldots (11.35)$$

11.6. Molar Partition Function

So far we have considered systems in which there were n individual distinguishable particles distributed in different energy-levels and f denoted the *molecular partition function*. But we have to deal with large-scale systems, in which quantities are taken in gm-moles.

Let us now take a system which may be supposed to be constituted of large number of smaller ones each with a gm-mole of the substance. That is, the individual unit here is not the molecule but a *mole*. Let the energy-levels allowed for the whole system be E_1, $E_2, \ldots E_i \ldots$, and let there be x such systems in all. In each of these there are, of course, N_0, Avogadro number of molecules. Then, the average energy E, of such a unit is

$$E = \frac{\Sigma x_i E_i}{\Sigma x_i}$$

If Z be the partition function of these systems, then $Z = \Sigma e^{-\frac{E_i}{kT}}$ Now, following the procedure as in the previous section (equation 11.28),

$$E = kT^2 \left[\frac{d \ln Z}{dT}\right] \quad \ldots (11.36)$$

where we designate Z as the *molar partition function.*

But we know, (eqn. 11.27) the energy of a gm-mole, [for convenience of writing, Avogadro number N_0 is written as N],

$$E = NkT^2 \left[\frac{d \ln f}{dT}\right] = kT^2 \left[\frac{d \ln f^N}{dT}\right]$$

This leads, on comparison, to the result, $Z = f^N$. The thermodynamic functions may then be written, as,

$$\left.\begin{aligned}
&(a)\ S = NkT \frac{d \ln f}{dT} + Nk \ln f \\
&\qquad = kT \frac{d \ln Z}{dT} + k \ln Z \\
&(b)\ A = -NkT \ln f = -kT \ln Z \\
&(c)\ G = -NkT\left[\ln f - \left(\frac{\partial \ln f}{\partial \ln V}\right)_T\right] \\
&\qquad = -kT\left[\ln Z - \left(\frac{\partial \ln Z}{\partial \ln V}\right)_T\right]
\end{aligned}\right\} \quad \ldots (11.37)$$

These relations would be true for systems where the molecules are all distinguishable and can occupy energy-levels without any restriction. Thus, these expressions would be valid, say, in the case of a crystal where the different atoms occupy fixed localised positions in the structure.

But in the case of indistinguishable particles, there would be some difference. We may proceed to consider it in the following fashion :

Suppose there are two distinguishable particles (a, b) which may be in three possible energy-levels $(\epsilon_1, \epsilon_2, \epsilon_3)$. Then the energy of the system may give rise to the following nine distributions:

(*i*) $E_1 = \epsilon_1(a) + \epsilon_1(b)$ (*iv*) $E_4 = \epsilon_1(a) + \epsilon_2(b)$ (*vii*) $E_7 = \epsilon_1(b) + \epsilon_2(a)$

(*ii*) $E_2 = \epsilon_2(a) + \epsilon_2(b)$ (*v*) $E_5 = \epsilon_1(a) + \epsilon_3(b)$ (*viii*) $E_8 = \epsilon_1(b) + \epsilon_3(a)$

(*iii*) $E_3 = \epsilon_3(a) + \epsilon_3(b)$ (*vi*) $E_6 = \epsilon_2(a) + \epsilon_3(b)$ (*ix*) $E_9 = \epsilon_2(b) + \epsilon_3(a)$

$$\begin{aligned}
\text{Then, } Z &= e^{-2\epsilon_1/kT} + e^{-2\epsilon_2/kT} + e^{-2\epsilon_3/kT} + 2e^{-\epsilon_1/kT}.e^{-\epsilon_2/kT} \\
&\quad + 2e^{-\epsilon_1/kT}.e^{-\epsilon_3/kT} + 2e^{-\epsilon_2/kT}.e^{-\epsilon_3/kT} \\
&= [e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + e^{-\epsilon_3/kT}]^2 = [\Sigma e^{-\epsilon/kT}]^2 = f^2
\end{aligned}$$

Now if the system contains N molecules (1 mole), then

$$Z = [\Sigma e^{-E_i/kT}] = \Sigma e^{-(\epsilon_1+\epsilon_2+\ldots\epsilon_i+\ldots\epsilon_N)/kT}$$

$$= \Sigma e^{-\epsilon_1/kT}.e^{-\epsilon_2/kT}\ldots e^{-\epsilon_N/kT}$$

(since each of these have N possible energy-levels)

$$\text{or} \qquad Z = (\Sigma e^{-\epsilon/kT})^N = f^N \qquad \ldots (11.38)$$

This is the result obtained earlier.

But if we presume the molecules to be indistinguishable, as in the case of a *perfect gas*, the relation above requires modification, for we have taken too many possible arrangements of the particles. In the case cited above, the state (*iv*) will be the same as (*vii*), when '*a*' and '*b*' are indentical. So the number of distribution would be much less. The N-particles in a gm-mole are all indistinguishable and these had $N!$ permutations among themselves in as many energy levels. We should therefore reduce the experession for Z by dividing the same with $N!$. Hence, for indistinguishable particles (a perfect gas), the molar partition function, Z in eqn. 11.37 should be replaced by $Z/N!$.

It is obvious that for systems of real gases, liquids, etc. such rigid relations will not be valid. For a perfect gas, the thermodynamic functions shall be [see equation 11.37]:

$$\left.\begin{aligned}
(a)\ S &= k\,ln\left(\frac{Z}{N!}\right) + kT\frac{d}{dT}\left(ln\frac{Z}{N!}\right)\\
&= k\,ln\,Z + kT\frac{d\,ln\,Z}{dT} - k\,ln\,N!\\
(b)\ A &= -kT\,ln\frac{Z}{N!} = -kT\,ln\,Z + kT\,ln\,N!\\
&= -kT\,ln\,Z + NkT\,ln\,N - NkT\\
&= -RT\left[ln\frac{f}{N} + 1\right]\\
(c)\ G &= A + PV = A + RT = -RT\,ln\frac{f}{N}
\end{aligned}\right\} \qquad \ldots (11.39)$$

11.7. The Third Law

It is now possible to make a statistical formulation of the Third Law.

From eqn. 8.4, $$S_T - S_0 = \int_0^T \frac{C_p}{T}\, dT$$

At very low temperatures, $$S_T - S_0 = \int_0^T \frac{C_v}{T}\, dT, \; (\because\; C_p \approx C_v)$$

Substituting partition function expression for C_v,

$$S_T - S_0 = \int_0^T \frac{1}{T}\left(\frac{dU}{dT}\right)_V dT$$

$$= \int_0^T \frac{1}{T}\frac{d}{dT}\left(kT^2 \frac{\partial\, ln\, Z}{\partial T}\right)_V dT$$

$$= kT\left(\frac{\partial\, ln\, Z}{\partial T}\right)_V + k\int_0^T \left(\frac{\partial\, ln\, Z}{\partial T}\right)_V dT$$

$$= \frac{U}{T} + k\, ln\, (Z)_T - k\, ln\, (Z)_0\,.$$

Equating the temperature-independent terms,

$S_o = k\, ln\, (Z)_o = k\, ln\, (f^N)_o = R\, ln\, (f)_o = R\, ln(g_o e^0) = R\, ln\, g_o$

As the temperature of the system is lowered, the value of degeneracy (g) declines because fewer distributions are compatible with the total energy. In the limit $T = 0°K$, only one distribution is compatible with a total energy of zero, every molecule is in the lowest level. In a perfect crystal at 0°K, there is only one arrangement, $g_o = 1$; hence its entropy, $S_o = 0$, which is the Third Law.

11.8. Partition Function for Molecules with Different Types of Energy

It is a fact that most often the molecules are associated with energy of different types. In expressing the partition function, all the types of energy have to be considered. Take a system containing N molecules (all of the same kind), all possessing different kinds of energy, say, translational, vibrational, rotational etc. Let the different types of energy be labelled α, β, γ, . . . etc.

The allowed energy-levels of the α-type are $\epsilon_{\alpha_1}, \epsilon_{\alpha_2}, \epsilon_{\alpha_3}, \ldots,$ for β-type are $\epsilon_{\beta_1}, \epsilon_{\beta_2}, \epsilon_{\beta_3}, \ldots,$ and so on.

The respective Boltzmann distributions will be

$$N_i^\alpha = \frac{N}{f_\alpha} e^{-\epsilon_{\alpha_i}/kT},\ N_i^\beta = \frac{N}{f_\beta} e^{-\epsilon_{\beta_i}/kT}, \ldots$$

where $f_\alpha, f_\beta \ldots$ etc., are the partition functions appropriate to $\alpha, \beta, \ldots$ types of energy.

The total energy (E) of the system is (see eqn. 11.28),

$$E = \Sigma\epsilon_{\alpha_i} . N_i^\alpha + \Sigma\epsilon_{\beta_i} N_i^\beta + \Sigma\epsilon_{\gamma_i} N_i^\gamma + \ldots$$

$$= NkT^2 \frac{d}{dT} ln\, f_\alpha + NkT^2 \frac{d}{dT} ln\, f_\beta + NkT^2 \frac{d}{dT} ln\, f_\gamma + \ldots$$

$$= NkT^2 \frac{d}{dT} ln\, (f_\alpha\, f_\beta\, f_\gamma \ldots).$$

If f is the net molecular partition function, when every molecule is capable of freely taking any number of types of energy, we may write,

$$E = NkT^2 \frac{d}{dT}\, ln\, f$$

∴ Comparing, $f = f_\alpha \cdot f_\beta \cdot f_\gamma \ldots$ . . . (11.40)

i.e., the net partition function is the product of the separate partition functions in respect of different types of energy associated with the molecules.

11.9. Partition Function for Translational Energy

The translational energy is also quantised, though the difference in the energy-levels are quite small. The only way in which a particle would exhibit periodicity in translational motion is in relation to its impacts on the walls of the container. Suppose in a cubical box of length l, a molecule is moving parallel to x-axis and repeats its motion each time it completes a path $2l$. Then $2l = n\lambda$, where n

is an integer and λ is the wavelength associated with the matter-wave. The translational energy (ϵ_x) along the x-axis is given by,

$$\epsilon_x = \tfrac{1}{2}mc_x^2 = \frac{1}{2m}\cdot p^2, \quad (p, \text{ the momentum})$$

or

$$\epsilon_x = \frac{1}{2m}\left(\frac{h}{\lambda}\right)^2, \quad \text{(using de-Broglie relation)}$$

$$= \frac{1}{2m}\left(\frac{hn}{2l}\right)^2 = \frac{n^2h^2}{8ml^2}$$

The molecular partition function due to translation in x-direction,

$$f_x = \Sigma e^{-\epsilon_x/kT} = \Sigma e^{\frac{-n^2h^2/8ml^2}{kT}}$$

Since energy levels are very close, we may assume continuity, so that

$$f_x = \int_0^\infty e^{\frac{-n^2h^2/8ml^2}{kT}}\, dn$$

Put $\dfrac{n^2h^2}{8ml^2kT} = a^2$, so that $dn = \dfrac{l}{h}\left(8mkT\right)^{\frac{1}{2}} da$

Hence
$$f_x = \frac{(8mkT)^{\frac{1}{2}}l}{h}\int_0^\infty e^{-a^2}\, da$$

$$= \frac{(8mkT)^{\frac{1}{2}}l}{h}\sqrt{\frac{\pi}{4}} = \frac{(2\pi mkT)^{\frac{1}{2}}l}{h}, \quad \left(\text{since} \int_0^\infty e^{-a^2}\, da = \tfrac{1}{2}\sqrt{\pi}\right)$$

Considering the translational motion in all the three directions, the molecular partition function for translation would be,

$$f = f_x^3 = \frac{(2\pi mkT)^{3/2}\, l^3}{h^3} = \frac{(2\pi mkT)^{3/2}V}{h^3} \quad \ldots (11.41)$$

For a perfect gas, the molar partition function would then be,

$$Z = f^N = \left[\frac{(2\pi mkT)^{3/2}V}{h^3}\right]^N$$

But for the indistinguishability of the molecules, it has to be modified as,

$$f^N = \frac{1}{N!}\left[\frac{(2\pi mkT)^{3/2}V}{h^3}\right]^N$$

$$= \left(\frac{e}{N}\right)^N\left[\frac{(2\pi mkT)^{3/2}V}{h^3}\right]^N, \text{ since, } N! = \left(\frac{N}{e}\right)^N; \text{(Stirling)}$$

$$= \left[\frac{(2\pi mkT)^{3/2}Ve}{Nh^3}\right]^N$$

Hence $$N\, ln f = N\, ln\left[\frac{(2\pi mkT)^{3/2}Ve}{Nh^3}\right]$$

Therefore $$f_{t_r} = \frac{(2\pi mkT)^{3/2}Ve}{Nh^3} \qquad \ldots (11.42)$$

Also, $$ln f_{t_r} = ln\frac{(2\pi mkT)^{3/2}Ve}{Nh^3} + ln\, T^{3/2}$$

or $$\frac{d\, ln f_{t_r}}{dT} = \frac{3}{2T} \qquad \ldots (11.43)$$

Hence from eqn. (11.35), for a monatomic gas,

$$C_v = R\frac{d}{dT}\left[T^2\frac{d\, ln f_{t_r}}{dT}\right] = R\frac{d}{dT}\left[T^2 \times \frac{3}{2T}\right] = \tfrac{3}{2}R \qquad \ldots (11.44)$$

Example : Calculate the translational partition function of an oxygen molecule confined to a 100 cm^3 vessel at 25°C.

In S. I units : $m_{o_2} = 16 \times 3.348 \times 10^{-27}\text{kg}$; $h = 6.626 \times 10^{-34}$ Js

$k = 1.381 \times 10^{-23}\ \text{JK}^{-1}$; $V = 100\ \text{cm}^3 = 10^{-4}\ m^3$

From eqn 11.41 $$f = \left[\frac{2\pi mkT}{h^2}\right]^{3/2} V$$

$$\therefore f = \left[\frac{2 \times 3.14 \times (16 \times 3.348 \times 10^{-27}\text{kg}) \times (298\text{K})\ (1.381 \times 10^{-23}\text{J.K}^{-1})}{(6.626 \times 10^{-34} J)^2}\right]^{3/2} \times (10^{-4}\text{m}^3)$$

$$= [32.87 \times 10^{20}\text{m}^{-2}]^{3/2} \times (10^{-4}\text{m}^3)$$

$$= 1.885 \times 10^{28}$$

It is thus seen that even at room temperature about 10^{28} quantum levels are thermally accessible for the oxygen molecule.

Monatomic gas

In a monatomic gas, vibration and rotation are absent ; only the translation is to be considered. Its internal energy or entropy can be easily evaluated from the partition function.

(*i*) The internal energy U,

$$U = NkT^2 \frac{d\,ln\,f}{dT} = RT^2 . \tfrac{3}{2}\frac{1}{T} = \tfrac{3}{2}\,RT, \text{ (from 11.43)}$$

(*ii*) The entropy S,

$$\begin{aligned} S &= U/T + Nk\,ln\,f, \text{ (neglecting statistical wt. factor)} \\ &= NkT\frac{d\,ln\,f}{dT} + Nk\,ln\,f \\ &= \tfrac{3}{2}\,R + R\,ln\,\frac{(2\pi mkT)^{3/2}Ve}{Nh^3} \\ &= R\,ln\,\frac{(2\pi mkT)^{3/2}\,Ve^{5/2}}{Nh^3} \qquad \ldots (11.45) \end{aligned}$$

or, $$S = R\left[ln\,(2\pi k/h^2)^{3/2} + ln\,\frac{M^{3/2}T^{3/2}e^{5/2}\,V}{N^{5/2}}\right]$$

$$\begin{aligned} &= [R\{5/2+3/2.ln\,2\pi k/h^2-5/2.ln\,N\}] + R[ln\,V+3/2.ln\,T \\ &\quad +3/2.ln\,M] \\ &= C_1 + R[ln V+3/2.ln\,T+3/2.ln\,M], \end{aligned}$$

where $C_1 = R(5/2+3/2.ln\,2\pi k/h^2-5/2.ln\,N)$
$= -11.073$ cal/degree

Again, since $RT/P = V$, we can write eqn. (11.45),

$$\begin{aligned} S &= R\,ln\,\frac{(2\pi mk)^{3/2}T^{5/2}e^{5/2}R}{Nh^3P} \\ &= R\,ln\,\frac{(2\pi M)^{3/2}(ek)^{5/2}T^{5/2}}{N^{3/2}h^3\,P}, \\ &\qquad (\because R=Nk;M = mN) \end{aligned}$$

or $$S = R\,ln\,\frac{(2\pi)^{3/2}\,(ek)^{5/2}}{N^{3/2}h^3} + 3/2.R\,ln M + 5/2.R\,ln\,T - Rln\,P, \qquad \ldots (11.46)$$

where the first term is -2.313 cal. degree^{-1}.

This is the well-known Sackur-Tetrode equation.

$$S = \tfrac{3}{2} R \ln M + \tfrac{5}{2} R \ln T - R \ln P - 2.313$$

The entropy increases with increasing mol. wt. and also with increasing temperature.

At standard pressure and temperature (25°C),

$$S = 6.86 \log_{10} M + 25.983 \text{ cal/degree.}$$

Monatomic gas	→	*He*	*Ne*	*A*
S (*e.u.*)	→	30.12	34.93	37.08

Problem : Calculate the entropy change of one mole of helium when it is heated from 300°K to 600°K at constant pressure.

$$S = R \ln \left[\frac{(2\pi M)^{3/2}(ek)^{5/2}}{N^{3/2}h^3 P} T^{5/2} \right]$$

$$= R \ln AT^{5/2}, \qquad \text{where } A = \frac{(2\pi M)^{3/2}(ek)^{5/2}}{N^{3/2}h^3 P}$$

Then $\quad S_{600} = R \ln (A . 600^{5/2}), \qquad S_{300} = R \ln (A . 300^{5/2})$

or $\quad \Delta S = R \ln \left(\frac{600}{300}\right)^{5/2} = \frac{5}{2} \times 1.98 \times 2.303 \log_{10} 2 = 3.43$ cal/degree-mole

11.10. Partition Function for Rotational Energy : Diatomic Molecules

From quantum mechanical principles, the rotational energy (ϵ_{rot}) for a diatomic molecule considered as a rigid rotator at the *j*th quantum level is given by

$$\epsilon_{rot} = j(j+1)\frac{h^2}{8\pi^2 I}; \quad [I = \text{moment of inertia, } \mu r^2]$$

Putting $B = h/8\pi^2 Ic$; $\epsilon_{rot} = j(j+1)Bhc$

The degeneracy g_j for the *j*th level is $(2j+1)$, which represents the number of possible orientations of the angular momentum vector with respect to the reference axis.

Hence the partition function (f_{rot}) for a rigid rotator is

$$f_{rot} = \sum g_j e^{-\epsilon_j/kT} = \sum_{j=0} (2j+1) e^{-j(j+1)Bhc/kT}$$

Assuming a continuum of rotational energy, the summation is replaced by integration, especially when $Bhc \leqslant kT$.

Putting $Bhc/kT = B'$,

$$f_{rot} = \int_0^\infty (2j+1)\, e^{-(j^2+j)B'}\, dj$$

Since $d(j^2+j) = (2j+1)\, dj$, hence

$$f_{rot} = \int_0^\infty e^{-(j^2+j)B'}\, d(j^2+j) = \frac{1}{B'} \int_0^\infty e^{-x}\, dx = \frac{1}{B'}$$

where $x = (j^2+j)B'$.

Thus the rotational partition function becomes

$$f_{rot} = \frac{1}{B'} = \frac{kT}{Bhc} = \frac{kT}{hc} \cdot \frac{8\pi^2 Ic}{h}$$

$$\text{or} \quad f_{rot} = \frac{8\pi^2 IkT}{h^2} \qquad \ldots (11.47)$$

For heteronuclear molecules like CO, NO, HCl, etc. this is valid. But in case of homonuclear molecules like $O^{16}O^{16}$, $N^{14}N^{14}$, etc, where the molecule when reversed becomes indistinguishable from the initial state, the partition function has to be divided by the symmetry number 2,

$$i.e. \quad f_{rot} = \frac{8\pi^2 IkT}{2h^2}$$

When the symmetry number is σ, $f_{rot} = \dfrac{8\pi^2 IkT}{\sigma h^2}$ . . . (11.48)

The molar rotational energy of a diatomic gas would then be

$$E_{rot} = NkT^2 \frac{d\, ln f_{rot}}{dT} = NkT^2 \frac{d}{dT} ln\,(8\pi^2 IkT/\sigma h^2) = NkT \qquad \ldots (11.49)$$

The rotational entropy (see eqn. 11.30),

$$S_{rot} = R\, ln\, f_{rot} + RT \frac{d\, ln f}{dT}$$

$$= R\, ln\, \frac{8\pi^2 IkT}{\sigma h^2} + RT \frac{d}{dT} ln \left(\frac{8\pi^2 Ik}{\sigma h^2}\, T\right)$$

$$= R\, ln \left(\frac{8\pi^2 IkT}{\sigma h^2}\right) + R = R\, ln \left(\frac{8\pi^2 IkTe}{\sigma h^2}\right) \qquad \ldots (11.50)$$

Collecting the constants together, this equation may be expressed as,

$$S_{rot} = R\,ln\,I + R\,ln\,T - R\,ln\,\sigma + R\times 89.40$$

This shows that the entropy increases with increasing moment of inertia as well as with increasing temperature.

Example : Estimate the rotational partition function of HCl gas at 300°K ; the moment of inertia is 2.66×10^{-40} g.cm^2.

$$\text{For HCl, } f_{\text{rot}} = \frac{8\pi^2 IkT}{\sigma h^2}$$

$$= \frac{8\times(3.14)^2\times2.66\times10^{-40}\times1.38\times10^{-16}\times300}{1\times(6.62\times10^{-27})^2}$$

$$= 19.76$$

11.11. Partition function for Vibrational Energy : Diatomic Molecules

At the nth quantum level, the vibrational energy of a diatomic molecule is given by $\epsilon_v = (n+\frac{1}{2})h\nu$, where ν is the fundamental frequency of vibration and n is an integer, 0, 1, 2, 3, 4, etc. Hence the vibrational partition function is

$$f_{vib} = \sum_{0}^{\infty} e^{-(n+\frac{1}{2})h\nu/kT}$$

$$= e^{-\frac{1}{2}h\nu/kT}\,[1+e^{-h\nu/kT}+e^{-2h\nu/kT}+\ldots+e^{-ih\nu/kT}+\ldots]$$

$$\text{or } f_{vib} = e^{-\frac{1}{2}h\nu/kT}(1-e^{-h\nu/kT})^{-1} \qquad \ldots (11.51)$$

The quantity $\frac{1}{2}h\nu/kT$ is indeed very small, and as a first approximate,

$$f_{vib} = (1-e^{-h\nu/kT})^{-1} \qquad \ldots (11.52)$$

The vibrational energy of a mole of diatomic gas from eqn. 11.27,

$$E_{vib} = RT^2\frac{d}{dT}\,ln\,f_{vib} = RT^2\,\frac{d}{dT}\left[ln\,e^{-h\nu/2kT}\left(1-e^{-h\nu/kT}\right)^{-1}\right]$$

$$= \frac{Nh\nu}{2} + Nh\nu\,\frac{e^{-h\nu/kT}}{1-e^{-h\nu/kT}} \qquad \ldots (11.53)$$

Example : Calculate the vibrational partition function of HCl at at 25°C. Given wave number $\omega = 2989$ cm^{-1}.

$$f_v = (1-e^{-h\nu/kT})^{-1} = (1-e^{-hc\omega/kT})^{-1} = (1-e^{-1.439\omega/T})^{-1}$$

$$= (1-e^{-1.439\times2989/298})^{-1} \approx 1.00$$

Example : The wave number of the normal vibration of Cl_2 is 556.9 cm^{-1}. Calculate the temp. at which 2.00% of the molecules will be in the 1st excited vibrational energy level.

If ω be the wave number,

$$E_1 = N_0 h\nu_0 = N_0 hc. \frac{1}{\omega} = (2.859 \times 556.9),$$

$$(\because N_0 hc = 2.859 \text{ cal-cm/mole})$$

Again, $n_0/n_1 = 98/2 = 49$

We know. $ln\, n_1/n_0 = -E_1/RT$

or $\log n_0/n_1 = E_1/(2.303 \times RT)$

or
$$T = \frac{E_1}{2.303 \times RT \log (n_0/n_1)}$$

$$= \frac{2.859 \times 556.9}{2.303 \times 1.98 \times \log 49} = 205°K.$$

An example to illustrate the calculation for distribution of population in different quantum levels is given here.

Example : At 25°C, the vibration energy levels of I_2 molecules have a constant difference of 214.6 cm^{-1}. Estimate the distribution of the molecules in the first four consecutive vbration levels.

Since the energy (ϵ) is given in wave numbers, the value of kT should be taken in same units ;

$$kT/hc = \frac{(1.38 \times 10^{-23} JK^{-1}) \times 298°K}{(6.626 \times 10^{-34} J\text{-}s)(3 \times 10^{10} cm\text{-}s^{-1})}$$

$$= 207\ cm^{-1}$$

Hence $\epsilon/kT = 214.6\ cm^{-1}/207\ cm^{-1} = 1.036$

$\therefore$ Partition function, $f_v = (1-e^{-\epsilon/kT})^{-1} = (1-e^{-1.036})^{-1} = 1.550$

The proportion of population in different j-levels will be given by

$$P_j = \frac{n_j}{N} = \frac{e^{-j\epsilon/kT}}{f_v} = \frac{e^{-j \times 1.036}}{1.55}$$

Putting $j = 0, 1, 2, 3,$ we have $P_0 = 0.645$, $P_1 = 0.230$, $P_2 = 0.083$, $P_3 = 0.029$

Using equation 11.52, the vibrational energy per mole would be

$$E_{vib} = RT^2 \frac{d}{dT} ln \left(1 - e^{-h\nu/kT}\right)^{-1} \approx RT \frac{h\nu/kT}{e^{h\nu/kT} - 1} \quad \ldots (11.54)$$

Again, work function, $A = -RT\, ln\, f_{vib}$

$$= -RT\, ln\, (1 - e^{-h\nu/kT})^{-1}$$

$$= RT\, ln\, (1 - e^{-h\nu/kT}) \qquad \ldots (11.55)$$

Hence, the vibrational entropy per mole,

$$S_{vib} = \frac{E_{vib} - A_{vib}}{T} = R\,\frac{h\nu/kT}{e^{h\nu/kT} - 1} - R\, ln\, (1 - e^{-h\nu/kT}) \qquad \ldots (11.56)$$

Electronic Partition Function : The electronic energy spacings are generally very large, and hence $e^{-\epsilon_e/kT}$-values are very small. Only at the ground state $\epsilon_e = 0$, hence in most cases,

$$f_{elec} = 1 \qquad \ldots (11.57)$$

In some cases, the atoms in the ground state may have a degeneracy, i.e. several states of the atom have the same energy. In such an event,

$$f_{elec} = g$$

This is observed in alkali metal atoms ; the two orientations of the unpaired electron spin lead to doublet ground states ($g = 2$). There are also a few other instances.

11.12. Diatomic Molecules

It is assumed that the rotational, vibrational and translational motions are independent of one another. As such at the ground electronic state ($f_e = 1$), the total molecular partition function of a diatomic molecule would be, for the gaseous phase,

$$f_{tot} = f_{tr} \cdot f_{rot} \cdot f_{vib}$$

Using eqns. (11.42, 11.47 and 11.52),

$$f_{tot} = \frac{g(2\pi mkT)^{3/2} Ve}{Nh^3} \cdot \frac{8\pi^2 IkT}{\sigma h^2} \cdot (1 - e^{-h\nu/kT})^{-1} \qquad \ldots (11.58)$$

Likewise, the energy per molecule, (eqns. 11.43, 11.49 and 11.54),

$$\epsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib}$$

$$= \frac{3}{2} kT + kT + \frac{h\nu}{e^{h\nu/kT} - 1} = \frac{5}{2} kT + kT\frac{h\nu/kT}{e^{h\nu/kT} - 1}$$

(*i*) The energy per gm-mole,

$$E = N_0\varepsilon = RT\left[5/2 + \frac{h\nu/kT}{e^{h\nu/kT}-1}\right] \qquad \ldots (11.59)$$

(*ii*) The entropy per gm-mole (eqns. 11.45, 11.50 and 11.56),

$$S = S_{tr} + S_{rot} + S_{vib}$$

$$= R\left[\frac{5}{2} + ln\left(\frac{g(2\pi mkT)^{3/2}V}{Nh^3}\right)\right] + R\left[ln\left(\frac{8\pi^2IkT}{\sigma h^2}\right) + 1\right]$$

$$+ R\,ln\left(\frac{h\nu/kT}{e^{h\nu/kT}-1}\right) - R\,ln\,(1 - e^{-h\nu/kT})$$

$$\approx R\left[5/2 + ln\left(\frac{g(2\pi mkT)^{3/2}V}{Nh^3}\right)\right] + R\left[ln\left(\frac{8\pi^2IkT}{\sigma h^2}\right) + 1\right]$$

$$+ R\left[1 - ln\left(\frac{h\nu}{kT}\right)\right] \qquad \ldots (11.60)$$

(*iii*) The heat-capacity, C_V per gm-mole, on differentiation of eqn. 11.59,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{5}{2}R + R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} \qquad \ldots (11.61)$$

Evidently, the evaluation of entropy from eqn. 11.60 would require the knowledge of I and ν, which are obtained from spectroscopic measurement. The entropy calculated thus is often called 'spectroscopic entropy'. These values really correspond to those calculated from the third law. Some instances are appended below.

TABLE : ENTROPIES AT 298°K IN JOULES/DEGREE

Molecules	Third law S	Spectroscopic S
A	154.8	154.8
Ne	146.4	146.2
HCl	186.2	186.8
CO	193.2	197.9
H_2	124.4	130.7
CH_4	186.2	186.8
Cd	168.0	167.2

The small discrepancy observed in the case of hydrogen and carbon monoxide is due to the presence of more than one indistinguishable symmetrical forms ; CO and OC, or of ortho and para hydrogen.

11.13. Equipartition of energy

The different kinds of energy possessed by a molecule are usually expressible in squared terms for each degree of freedom. Thus, the kinetic energy is of the form $\frac{1}{2}mc_x^2$, rotational energy, $\frac{1}{2}Iw^2$, vibrational energy $\frac{1}{2}kx^2 + \frac{1}{2}mu^2$, and so on. Let there be r such terms, associated with the energy of a molecule. Then, the energy ϵ of a molecule

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 + \ldots \epsilon_r$$

$$= b_1x_1^2 + b_2x_2^2 + b_3x_3^2 + \ldots + b_rx_r^2$$

The partition function of the molecule,

$$f = f_1 . f_2 . f_3 . f_4 \ldots f_r$$

$$= \int_0^\infty e^{-\beta b_1 x_1^2} dx_1 \int_0^\infty e^{-\beta b_2 x_2^2} dx_2 \int_0^\infty e^{-\beta b_3 x_3^2} dx_3 \ldots \int_0^\infty e^{-\beta b_r x_r^2} dx_r$$

To simplify,

$$\text{let } y_1^2 = \beta x_1^2, \quad dy_1 = \beta^{1/2} dx_1, \quad i.e., \; dx_1 = \frac{dy_1}{\beta^{1/2}}$$

$$\therefore \quad \int_0^\infty e^{-\beta b_1 x_1^2} dx_1 = \int_0^\infty \frac{e^{-b_1 y_1^2}}{\beta^{1/2}} dy_1 = \beta^{-1/2} \int_0^\infty e^{-b_1 y_1^2} dy_1$$

Putting Q_1 for the integral on the right, $= \beta^{-1/2} Q_1$

$$\therefore \quad f = \beta^{-1/2} Q_1 . \; \beta^{-1/2} Q_2 . \; \beta^{-1/2} Q_3 \ldots \beta^{-1/2} Q_r$$

$$= \beta^{-r/2} Q, \quad (\text{where } Q = Q_1 . Q_2 . Q_3 . \ldots)$$

It is to be remembered that $Q_1, Q_2 \ldots$ etc. and hence Q, would not contain β.

Now, $$\epsilon = \frac{U}{N} = kT^2 \frac{d \ln f}{dT} = -\frac{d \ln f}{d(1/kT)} = -\frac{d}{d\beta} \ln f$$

Hence, $$\epsilon = -\frac{d}{d\beta} \ln (\beta^{-r/2} . Q) = \frac{d}{d\beta} [r/2 . \ln \beta - \ln Q]$$

$$= \frac{r}{2\beta} = \frac{r}{2} kT, \quad (\because \; \beta = 1/kT)$$

That means, that if the energy could be expressed as sum of r squared terms, the average energy ϵ is $r \times \frac{1}{2}kT$. Hence, for each degree of freedom, the energy is $\frac{1}{2}kT$. This is the principle of the equipartition of energy.

But such conditions are *not* fulfilled in some instances. For example in the case of a gas in a gravitational field, where potential energy is not a squared term but mgh ; the mean gravitational pot. energy is *not* $\frac{1}{2}kT$. Similarly, in those cases where energy taken up is quantised, the energy associated with them is not a linear function of the temperature.

In the case of crystals, say of metals, the atoms have only vibratory motion. The vibration may occur in three directions and each mode has two degrees of freedom.

$$\text{Hence, } \epsilon = \tfrac{1}{2}kT \times 3 \times 2 = 3kT, \quad \text{or } E = 3RT \approx 6T$$

$$\therefore \quad C_v = \left(\frac{\partial E}{\partial T}\right)_v \approx 6 \text{ cal, which is Dulong-Petit law.}$$

It means heat-capacity should be independent of temperature. But in fact, considerable variation with temperature has been noticed. That is, the principle of equipartition has failed.

The heat capacity of solids has been accounted for with quantal principles as shown below.

11.14. Heat capacity of solids. (*i*) Einstein Equation. The atoms of the crystal arranged in a definite pattern have only vibrational motion, the electronic levels assumed to be unexcited. For each atom, there are three vibrational degrees of freedom, so that for a crystal of N atoms (1 gm-mole), there are $3N$ degrees of freedom. The vibrational motion is considered harmonic, so that an oscillating atom at the nth level will have the energy, $\epsilon = (n + \frac{1}{2})h\nu$, where ν is the fundamental frequency.

A fairly satisfactory quantal treatment of the specific heat of such a solid was first proposed by Einstein (1907). He considered that the N atoms of the crystal were all independently vibrating with a common frequency ν. Then the partition function for the whole crystal is given by,

$$\begin{aligned} f^N &= \Sigma[e^{-(n+\frac{1}{2})h\nu/kT}]^{3N} \\ &\approx [e^{-\frac{1}{2}h\nu/kT}(1-e^{-h\nu/kT})^{-1}]^{3N} \end{aligned}$$

or $$\ln f = -\tfrac{3}{2}\frac{h\nu}{kT} - 3\ln\left(1-e^{-h\nu/kT}\right)$$

Applying equation (11.53), the energy will be given by,

$$E = \tfrac{3}{2}Nh\nu + \frac{3Nh\nu e^{-h\nu/kT}}{1-e^{-h\nu/kT}}$$

$$= \tfrac{3}{2}Nh\nu + 3N\frac{h\nu}{e^{h\nu/kT}-1}$$

The heat-capacity, $C_v = \left(\frac{\partial E}{\partial T}\right)_V$

or $$C_v = 3Nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT}-1)^2} \quad \ldots (11.62)$$

This is *Einstein Equation*,

The Einstein equation gives temperature curves very similar to the experimental ones. Of course, the value of ν is determined from experimental results empirically. In fact, when temperature is high, that is, $h\nu/kT$ is quite small, we have, $C_V = 3R$. This is in agreement with the classical theory and the Dulong and Petit Law. Again, as T tends to zero, C_V also tends to zero, a conclusion in general agreement with experimental facts. But in the lower ranges of temperature, the calculated values (from Einstein equation) fall more rapidly than do the experimental values. This disagreement is due to the neglect of the mutual interatomic forces. It was Debye (1912) who developed a modified equation which gave a very satisfactory agreement with experiment over the entire temperature range.

(*ii*) **Debye's Equation.** Debye suggested that (*i*) a solid is to be assumed as an elastic body, and the vibrations of the whole should be considered (*ii*) the $3N_0$-modes of vibration (in a gm-atom) of a monatomic solid are not all identical, as assumed by Einstein, but are distributed among a spectrum of frequencies. The frequencies range from zero ($\nu = 0$) to a maximum frequency ν_m, ($\nu = \nu_m$), which is a characteristic of the solid. Debye's ν_m is different from Einstein's ν and it can be shown that $\nu_m = \frac{4}{3}\nu$.

Now, it is known that if the total number of ways, z, in which an elastic medium of volume V can vibrate with a frequency ν, then dz between the frequency range $\nu + d\nu$ and ν will be given by

$$dz = \frac{4\pi V}{c^3}\nu^2 d\nu \cdot$$

If we take a gm-atom of the solid elements, containing N_0 atoms, the total number of vibrations possible will be $3N_0$. Remembering the frequency-range $\nu = 0$ to $\nu = \nu_m$, we have

$$\int dz = \int_0^{\nu_m} \frac{4\pi V}{c^3}\nu^2 d\nu = \frac{4\pi \nu_m^3}{3c^3} V = 3N_0$$

Eliminating V, we have, $dz = \frac{9N_0}{\nu_m^3}\nu^2 d\nu$

Now the vibrational partition function,

$$f_v = e^{-\frac{1}{2}h\nu/kT}(1 - e^{-h\nu/kT})^{-1}$$

or $$\ln f_v = -\frac{h\nu}{2kT} - \ln(1 - e^{-h\nu/kT})$$

The partition function of the whole crystal may be obtained by attaching to each frequency the partition function of the single oscillation, *i.e.*,

$$N \ln f = \int_0^{\nu_m} \phi(\nu)[-\tfrac{1}{2}h\nu/kT - \ln(1 - e^{-h\nu/kT})]d\nu$$

$$= \frac{9N}{\nu_m^3}\int_0^{\nu_m}[-\tfrac{1}{2}h\nu/kT - \ln(1 - e^{-h\nu/kT})]\nu^2 d\nu$$

$$= -\frac{9}{8}\frac{Nh\nu_m}{kT} - 3N\ln(1 - e^{-h\nu/kT}) + \frac{3N}{\nu_m^3}\int_0^{\nu_m}\frac{\frac{h\nu^3}{kT}e^{-h\nu/kT}}{1 - e^{-h\nu/kT}}d\nu$$

At sufficiently low temperature, the second term is very small and negligible.

Putting $\frac{h\nu}{kT} = x$, *i.e.*, $d\nu = (kT/h)dx$

$$N \ln f = -\frac{9}{8}\frac{Nh\nu_m}{kT} + 3N\left(\frac{kT}{h\nu_m}\right)^3 \int_0^{\infty}\frac{x^3}{e^x - 1}dx$$

$$= -\frac{9}{8}\frac{Nh\nu_m}{kT} + 3N\left(\frac{kT}{h\nu_m}\right)^3 \frac{\pi^4}{15}$$

Now, substituting this in equation (11.27), the energy is

$$E = \frac{9}{8} Nh\nu_m + \frac{3\pi^4}{5} Nk \left(\frac{k}{h\nu_m}\right)^3 T^4$$

Therefore, the heat capacity would be,

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{12\pi^4}{5} Nk \left(\frac{k}{h\nu_m}\right)^3 T^3 \ldots (11.63)$$

This is Debye's specific-heat relation at low temperatures. Expressing $\frac{h\nu_m}{k} = \theta_D$, the equation may be written as

$$C_V = \frac{12\pi^4}{5} R \frac{T^3}{\theta_D{}^3} = \frac{464.6}{\theta_D{}^3} T^3$$

11.14a. Mixing of perfect gases

Suppose n_1 molecules of a perfect gas A having a volume v_1 be allowed to mix with n_2 molecules of another perfect gas B having a volume v_2. The molecules of A and B are distinguishable. The molecules of A alone are indistinguishable and the same is true of the molecules of B. The two types of molecules do not interact. The temperature (T) and the pressure (P) remain constant throughout.

(*i*) *Pressure* : The grand partition function of the mixture of gases is given as,

$$Z = f_1{}^{n_1} f_2{}^{n_2} = \left(\frac{\phi Ve}{n_1}\right)^{n_1} \left(\frac{\phi Ve}{n_2}\right)^{n_2}$$

where V is the total volume and ϕ written for

$$\left[\frac{(2\pi mkT)^{3/2}}{h^3} + f_{rot} + f_{vib}\right].$$

As the temperature is fixed, the partition functions for rotation and vibration are supposed to remain unaltered. The molecules of each gas are also supposed to move quasi-independently of each other.

Using equation 11.32,

$$P = kT\left(\frac{d\,ln\,Z}{dV}\right)_{T,n_1,n_2}$$

$$= kT(n_1/V + n_2/V) = n_1kT/V + n_2kT/V$$

$$\therefore P = P_1 + P_2$$

where P_1, P_2 are partial pressures of the two gases in the mixture. This is Dalton's Law.

(*ii*) *Entropy* : In the mixture, the total number of molecules $n = (n_1 + n_2)$ and the total volume $V = (v_1+v_2)$. If W represents the thermodynamic probability of distribution of the mixture,

then $$S = k\,ln\,W = k\,ln\,\frac{n!}{n_1!\,n_2!}$$

It relates to the increase in configurational entropy in the mixing of the two different types. Applying Stirling's rule of approximation,

$$S_{mix} = k[n\,ln\,n - n - n_1\,ln\,n_1 + n_1 - n_2\,ln\,n_2 + n_2];$$

(the last four terms account for the entropies of individual components)

$$= k[(n_1 + n_2)\,ln\,n - n_1\,ln\,n_1 - n_2\,ln\,n_2]$$

$$= -k\left[n_1\,ln\frac{n_1}{n} + n_2\,ln\frac{n_2}{n}\right]$$

$$= -k[n_1\,ln\,x_1 + n_2\,ln\,x_2]$$

where x_1, x_2 are the mole-fractions of the two gases present.

$$\therefore S_{mix} = -kN_o\left[\frac{n_1}{N_o}\,ln\,x_1 + \frac{n_2}{N_o}\,ln\,x_2\right]$$

$$= -R[v_1\,ln\,x_1 + v_2\,ln\,x_2]$$

where N_o = Avogadro numbers and v_1, v_2 are the moles of the two gases.

In general, for a number of gases,

$$S_{mix} = -R\Sigma v_i\,ln\,x_i$$

This is the same relation as obtained from classical thermodynamics (see. eqn. 5.23).

11.15. Quantum Statistics

We have so far attempted to predict the behaviour and properties of systems from the Boltzmann statistics, often called the 'classical' statistics. The classical statistics is quite suitable for crystalline solid systems. At low densities of gases, the Boltzmann distribution Law is fairly satisfactory but when the density is high, the classical statistics shows little agreement with experimental facts. The classical statistics also fails to explain the behaviour of 'electron-gas' in metals or that of the photons. These anomalies led to the formulation of quantum statistics developed in two ways for different systems : (*i*) Bose-Einstien statistics and (*ii*) Fermi-Dirac statistics. Both of them are concerned with indistinguishable particles. It would however been seen later that the Boltzmann distribution Law follows from either the *B-E* statistics or the *F-D* statistics, provided the density of the particles in the system is comparatively low. For real gases at ordinary pressures, corrections with any quantum statistics are quite small and the *M-B* statistics would be appropriate enough. (See Sec. 11-1)

11.16. The Bose-Einstein statistics.

In classical distribution the particles are labelled, i.e., distinguished from one another. If two particles interchange their positions (or energy states), a new complexion would occur. But in Bose-Einstein statistics, we start with identical particles which are indistinguishable. Thus, the interchange of two particles between two energy-states will not give rise to a new complexion.

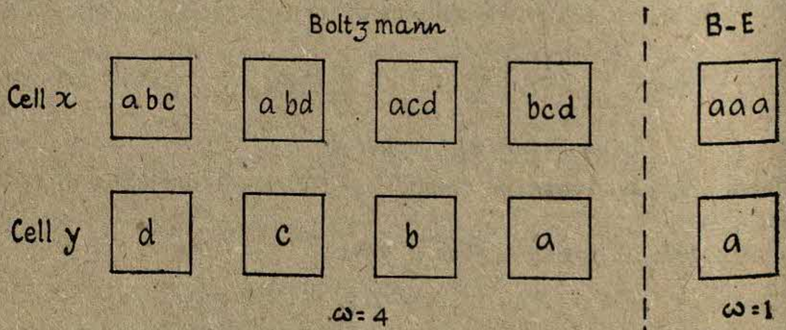

Fig. 11*a*

Suppose there are four particles distributed between two cells *x* and *y*, three in *x* and one in *y*. They would give rise to 4 complexions if they are distinguishable (Boltzmann) and only one complexion, if indistinguishable (Bose-Einstein) (Fig. 11*a*).

It must be recognised that the available energy states under usual conditions are much larger than the number of molecules (Eqn. 5.27). Let us consider a small energy range so that all the molecules may be supposed to have the same energy. The number of energy states even within this range would be quite large. The molecules may be distributed in these states without any restriction.

To illustrate in the example cited just before, suppose the cells are divided into four sections by partitions, the sections representing the energy states. The following distributions are then possible.

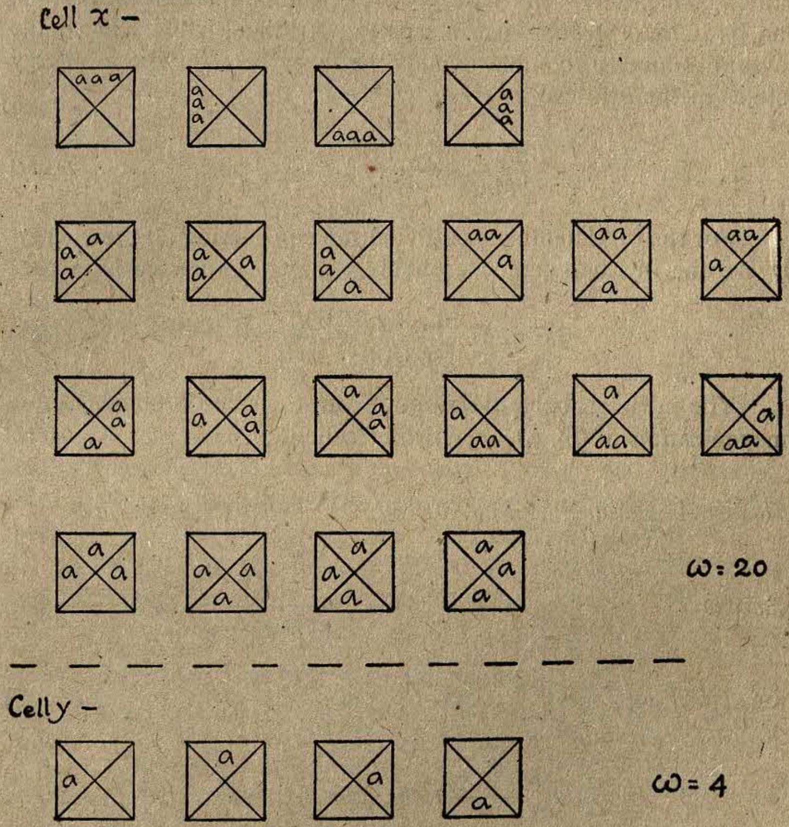

Fig. 11*b*.

Altogether then there are 20 possible distribution for three particles in cell x and 4 ways of distribution of one particle in cell y. So the total number of possible distribution is $20 \times 4 = 80$, (Fig 11*b*).

An attempt may now be made for a general expression of the distribution of particles under these conditions. Suppose there are n_i particles each with energy ϵ_i in the i-th level in which there are g_i states of energy. The degeneracy is g_i. Hence (g_i-1) partitions would be required to place n_i particles in g_i sections, each section corresponding to an energy state. The problem is to distribute n_i particles into g_i sections without any restriction. The permutation of n_i particles and $(g_i - 1)$ partitions simultaneously is given by $(n_i + g_i - 1)!$ But this includes also the permutation of n_i particles amongst themselves and also $(g_i - 1)$ partitions amongst themselves, as both these groups are internally indistinguishable. Hence the actual number of complexions of the n_i particles in the g_i energy states in the i-th level is given by

$$\frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!} \qquad \ldots (11.64)$$

For the total number of distribution considering all the energy-levels, the thermodynamic probability may be expressed as

$$W = \prod_i \frac{(n_i + g_i - 1)!}{(n_i)!\,(g_i - 1)!} \qquad \ldots (11.65)$$

The most probable distribution can then be obtained from a maximization of W. Using Stirling's theorem,

$$ln\, W = \sum_i \left[(n_i+g_i-1)\, ln\,(n_i+g_i-1) - n_i\, ln\, n_i - (g_i-1)\, ln(g_i-1)\right]$$

$$\therefore\ d\, ln\, W = \sum_i \left[ln\,(n_i+g_i-1) + \frac{n_i+g_i-1}{n_i+g_i-1} - ln\, n_i - \frac{n_i}{n_i}\right] dn_i$$

$$\text{or } d\, ln\, W = \sum_i ln\left(\frac{n_i+g_i-1}{n_i}\right) dn_i \qquad \ldots (11.66)$$

$$\approx \sum_i ln\left(\frac{n_i+g_i}{n_i}\right) dn_i, \text{ since } g_i \text{ is much larger than unity.}$$

At the maximum, $d\, ln\, W = 0$, hence

$$\sum_i ln\left(1 + \frac{g_i}{n_i}\right) dn_i = 0 \qquad \ldots (11.67)$$

As in the derivation of the Boltzmann law, we must remember,

$$\Sigma \epsilon_i \, dn_i = 0 \qquad \ldots (A)$$

$$\Sigma \, dn_i = 0 \qquad \ldots (B)$$

Multiply (B) by α and (A) by β and subtruct (11.67), when

$$\sum \left[\alpha + \beta\epsilon_i - ln \left(1 + \frac{g_i}{n_i} \right) \right] dn_i = 0$$

Since $dn_i \neq 0$, the expression within the square bracket would be individually zero for any level i.

or
$$ln \left(|1 + \frac{g_i}{n_i} \right) = \alpha + \beta\epsilon_i$$

or
$$\frac{g_i}{n_i} = e^{\alpha} e^{\beta\epsilon_i} - 1$$

$$\therefore \qquad n_i = \frac{g_i}{e^{\alpha} e^{\beta\epsilon_i} - 1} \qquad \ldots (11.68)$$

This is *Bose-Einstein distribution Law.*

11.17. The Fermi-Dirac Statistics

In the Boltzmann or in the Bose-Einstein statistics, there was no restriction as to the number of particles present in any energy-state. But in applying the distribution law to particles, like electrons, the Pauli Exclusion principle is invoked. That is, two particles in an atom cannot have the same energy-state. It means that not more than one particle can be assigned to a particular energy-state.

In the example previously taken, in which four particles were distributed in two cells, with three particles in cell x and one in cell y, we have the distributions as in Fig. 11c, remembering that

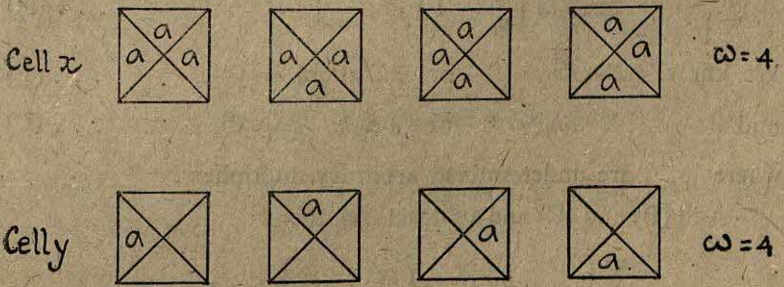

Fig. 11c

each cell is divided into 4 compartments. The total number of possible arrangements, with the restriction that one particle only can occupy a compartment, is $4 \times 4 = 16$.

Let there be n_i particles of energy ϵ_i in which there are g_i energy-states. Remembering that all particles are indistinguishable and that one state can have one particle, the number of ways n_i particles can be distributed among g_i - states in that level is given by

$$\frac{(g_i)!}{(n_i)!\,(g_i - n_i)!}$$

In considering all the energy levels, the theromodynamic probability would be,

$$W = \Pi \frac{(g_i)!}{(n_i)!\,(g_i - n_i)!}$$

Hence $$ln\, W = \sum_i [ln(g_i)! - ln(n_i)! - ln(g_i - n_i)!]$$

$$= \sum_i [g_i\, ln\, g_i - n_i\, ln\, n_i - (g_i - n_i)\, ln\, (g_i - n_i)]$$

Using Stirling's theorem,

Since g_i is constant,

$$d\, ln\, W = \sum_i ln \left(\frac{g_i - n_i}{n_i}\right) dn_i$$

For the most probable distribution, $d\, ln\, W = 0$.

$$\therefore \sum_i ln \left(\frac{g_i - n_i}{n_i}\right) dn_i = 0$$

$$\text{or } \sum_i ln \left(\frac{g_i}{n_i} - 1\right) dn_i = 0 \qquad \ldots (A)$$

We know, $\Sigma \epsilon_i\, dn_i = 0$, or $\beta \Sigma\, \epsilon_i\, dn_i = 0$ . . . (B)

and $\Sigma\ dn_i = 0$ or $\alpha \Sigma\, dn_i = 0$ . . . (C)

where α, β are undetermined arbitrary multipliers.

Add (B) and (C) and subtract (A), then

$$\sum_i \left[\alpha + \beta\epsilon_i - ln\left(\frac{g_i}{n_i} - 1\right)\right] dn_i = 0$$

Since $dn_i \neq 0$, and α, β are arbitrary constants, the terms within each of the parantheses would be zero.

$$\therefore \quad \alpha + \beta \epsilon_i - ln\left(\frac{g_i}{n_i} - 1\right) = 0$$

$$\text{or} \quad \frac{g_i}{n_i} = e^{\alpha} e^{\beta \epsilon_i} + 1$$

$$\text{i.e.} \quad n_i = \frac{g_i}{e^{\alpha} e^{\beta \epsilon_i} + 1} \qquad \ldots (11.69)$$

This is the *Fermi-Dirac distribution Law.*

In comparing the three statistics, we may write,

Maxwell-Boltzmann : $n_i = \dfrac{g_i}{e^{\alpha} e^{\beta \epsilon_i}}$

Bose-Einstein : $n_i = \dfrac{g_i}{e^{\alpha} e^{\beta \epsilon_i} - 1}$

Fermi-Dirac : $n_i = \dfrac{g_i}{e^{\alpha} e^{\beta \epsilon_i} + 1}$

Rearrangement of these expressions leads to

Maxwell-Boltzmann : $\dfrac{g_i}{n_i} = e^{\alpha} e^{\beta \epsilon_i}$

Bose-Einstein : $\dfrac{g_i}{n_i} + 1 = e^{\alpha} e^{\beta \epsilon_i}$

Fermi-Dirac : $\dfrac{g_i}{n_i} - 1 = e^{\alpha} e^{\beta \epsilon_i}$

When the value of g_i/n_i is much greater than unity, which is often the case, both the quantum statistics reduces to the classical distribution.

11.18. Maxwell-Boltzmann Distribution Function for Translational Energy

The wave functions for the translational energy of a particle in a box is given by the Schrödinger's equation as

$$\frac{\partial^2 \psi_x}{\partial x^2} + \frac{\partial^2 \psi_y}{\partial y^2} + \frac{\partial^2 \psi_z}{\partial z^2} = -\frac{8\pi^2 m}{h^2} \epsilon_{tr} \psi$$

ϵ_{tr} is the total translational energy of the particle. ψ_x, ψ_y and ψ_z are the wave functions along the co-ordinates x, y and z. Admitting separability, the wave function for one component, say in the x-direction, may be written as

$$\frac{d^2\psi_x}{dx^2} = \frac{-8\pi^2 m}{h^2} \epsilon_x \psi_x$$

The solution to this equation has been found to be

$$\epsilon_x = \frac{h^2}{8m}\left(\frac{n_x}{a}\right)^2 \qquad \ldots (A)$$

where n_x is a positive integer (not zero) and is called the translational quantum number in the x-direction.

Extending this treatment to the other two directions, the total translational energy would be

$$\epsilon_{tr} = \frac{h^2}{8m}\left[\left(\frac{n_x}{a}\right)^2 + \left(\frac{n_y}{b}\right)^2 + \left(\frac{n_z}{c}\right)^2\right] \qquad \ldots (B)$$

where a, b and c are the dimensions of the box in the three directions, and n_x, n_y and n_z are the respective quantum numbers.

To simplify, suppose the box be a cubic one with each side equal to 'a'. Then

$$\epsilon_{tr} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \qquad \ldots (C)$$

The translational quantum numbers taken as unity would give the smallest translational energy, $\epsilon_0 = 3h^2/8ma^2$. It is indeed extremely small and of the order of 10^{-18} cal/mole. Moreover the energy difference between successive levels is also very small. The energy-levels are hence very close almost producing a continuum.

The number of energy states (g) having the same translational energy (*i.e.* same level) is given by those states for which $(n_x^2 + n_y^2 + n_z^2)$ are the same in a box of cubic dimensions. Plotted in a three-dimensional graph only those points for which n_x, n_y and n_z are not only positive but also integral would represent the desired quantum states.

Putting $r^2 = n_x^2 + n_y^2 + n_z^2$,

$$\epsilon_{tr} = \frac{h^2}{8ma^2} r^2 \qquad \ldots (C)$$

It is evident that all points in an octant of a sphere which are at a radius r from the centre would have the same energy ϵ.

From (C), $$dr = \frac{a}{h}(8m)^{\frac{1}{2}}\,\tfrac{1}{2}\,\epsilon^{-\frac{1}{2}}d\epsilon \qquad \ldots \text{(D)}$$

(the suffix *tr* is dropped for convenience of writing)

If we have two spheres of radii r and $(r + dr)$, [corresponding to energy values ϵ and $(\epsilon + d\epsilon)$], the volume of the spherical shell between the two spheres is $4\pi r^2 dr$. The desired points satisfying the positive and integral values of the translational quantum numbers must be in one octant of the sphere. The volume of the shell in this octant represents the difference of the energy states dg. Or,

$$dg = \tfrac{1}{8}\times 4\pi r^2 dr = \tfrac{1}{2}r^2 dr \qquad \ldots \text{(E)}$$

Substituting dr from (D) in (E),

$$dg = \tfrac{1}{2}\pi\left(\frac{8ma^2\epsilon}{h^2}\right)\left(\frac{a}{h}\right)(8m)^{\frac{1}{2}}\,\tfrac{1}{2}\epsilon^{-\frac{1}{2}}d\epsilon$$

or $$dg = 2\pi\left(\frac{a}{h}\right)^3(2m)^{3/2}\epsilon^{\frac{1}{2}}d\epsilon$$

$$= \frac{2\pi V\,(2m)^{3/2}\,\epsilon^{\frac{1}{2}}}{h^3}d\epsilon, \qquad (\text{since } a^3 = V) \qquad \ldots \text{(F)}$$

The Maxwell-Boltzmann statistics may then be employed to determine the translational energy distribution amongst the various particles.

$$n_i = \frac{ng_i e^{-\beta\epsilon_i}}{f},$$

where f = translational partition function $= (2\pi mkT)^{3/2}\,V/h^3$ and $\beta = 1/kT$.

Putting $n_i/n = p_i$, the probability or fraction of particles associated with energy ϵ_i

So, $$p_i = \frac{g_i e^{-\beta\epsilon_i}}{f}$$

or $$dp_i = \frac{e^{-\beta\epsilon_i}}{f}\,dg_i$$

Since it is necessary to apply this to practically a continuous distribution, it could be generally presented as

$$dp = \frac{e^{-\beta\epsilon}}{f}\,dg$$

$$= \frac{2\pi e^{-\beta\epsilon}V\,(2m)^{3/2}\epsilon^{\frac{1}{2}}d\epsilon}{h^3\times(2\pi mkT)^{3/2}V/h^3}\text{, (from F and G)}$$

or
$$dp = \frac{2\epsilon^{\frac{1}{2}}e^{-\epsilon/kT}\,d\epsilon}{\pi^{1/2}(kT)^{3/2}} \qquad \ldots \text{(H)}$$

This is the distribution desired. It gives the fraction of particles having energies between ϵ and $(\epsilon + d\epsilon)$.

This relation can be used to find out the distribution of velocities as well. Now

$$\epsilon = \tfrac{1}{2}mc^2 \quad \text{or} \quad d\epsilon = mcdc.$$

Introducing these in equation H, we have

$$dp_c = \frac{2(\frac{1}{2}mc^2)^{\frac{1}{2}}\,e^{-mc^2/2kT}.\,mcdc}{\pi^{1/2}\,(kT)^{3/2}}$$

or
$$\frac{1}{n}\,dn_c = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}c^2\,e^{-mc^2/2kT}\,dc. \qquad \ldots \text{(I)}$$

This is the velocity distribution between c and $(c + dc)$.

11.19. The Electron Gas

The electrons in a metal moving freely are comparable with the molecules of an ideal gas and are generally referred as the 'electron gas'. Like monatomic molecules of an ideal gas, these electrons would have allowed energy levels with degeneracies for their translational motions. It is therefore possible to find out the translational energy distribution in different energy states with the help of our statistical methods. The application of *M-B* statistics however does not yield satisfactory results and the electron gas is found to be governed by *F-D* statistics. Hence any energy state would have only one electron.

The Fermi-Dirac distribution law gives (Sec. 11-17),

$$n_i = \frac{g_i}{e^{\alpha}e^{\beta\epsilon_i}+1} = \frac{g_i}{Ae^{\beta\epsilon_i}+1} \qquad \ldots (11.69)$$

where $A = e^{\alpha}$.

As in the case of an ideal gas, the degeneracy in a level of the translational energy mode is given by (eqn. F, Sec 11-18).

$$\begin{aligned} dg &= 2\times[2\pi V(2m)^{3/2}\epsilon^{\frac{1}{2}}d\epsilon/h^3] \\ &= \frac{\pi}{2}\,\frac{(8m)^{3/2}V}{h^3}\epsilon^{\frac{1}{2}}d\epsilon \qquad \ldots (i) \end{aligned}$$

The factor 2 is used to account for the two types of spin of an electron leading to two energy states. Since one electron is present in each state, the integration of this equation (*i*) would give the total number of electrons. Hence

$$\int dg = n = \frac{\pi}{2}\,\frac{(8m)^{3/2}V}{h^3}\int \epsilon^{\frac{1}{2}}d\epsilon \qquad \ldots (ii)$$

Again from eqn. (11-69) above,

$$dn_i = \frac{dg_i}{Ae^{\beta\epsilon_i}+1}$$

Replacing dg_i by dg and dn_i by dn for any level and substituting dg by equation (*i*), we have the number of electrons having energy between ϵ and $\epsilon + d\epsilon$,

$$dn_\epsilon = \frac{\pi}{2}\,\frac{(8m)^{3/2}V}{h^3}\cdot\frac{\epsilon^{\frac{1}{2}}d\epsilon}{Ae^{\beta\epsilon_i}+1} \qquad \ldots (iii)$$

The integral of this equation would also lead to the total number of electrons. That is,

$$n = \frac{\pi}{2}\,\frac{(8m)^{3/2}V}{h^3}\int_0^\infty \frac{\epsilon^{\frac{1}{2}}d\epsilon}{Ae^{\beta\epsilon_i}+1} \qquad \ldots (iv)$$

But the uncertainty of 'A' makes the integration difficult. An attempt to evaluate A is made with some presumptions. Suppose the electrons are distributed, one in each state, from the ground state up to a maximum level. This maximum level up to which electrons are distributed is called the *Fermi level* and let the maximum translational energy at the Fermi level (called 'Fermi energy') be denoted by ϵ_m. Now ϵ_m can be ascertained from integration of eqn. (*ii*) between the limits $\epsilon = 0$ and $\epsilon = \epsilon_m$.

The total number of molecules,

$$n = \frac{\pi}{2}\frac{(8m)^{3/2}V}{h^3}\int_0^{\epsilon_m}\epsilon^{\frac{1}{2}}d\epsilon$$

or $$n = \frac{\pi}{3}\frac{(8m)^{3/2}V}{h^3}\epsilon_m{}^{3/2} \qquad \ldots (v)$$

i.e. $$\epsilon_m = \frac{h^2}{8m}\left(\frac{3n}{\pi V}\right)^{2/3} \qquad \ldots (vi)$$

It is reasonably assumed that each monovalent metal atom contributes one electron to the electron gas, each divalent metal atom contributes two electrons to the electron gas, etc. The Fermi energy can then be calculated from eqn. (*vi*).

For silver, $\frac{n}{V} = 5.86 \times 10^{28}$ free electrons per m^3. Using standard values of h and m in *S-I* units,

$$\epsilon_{m(Ag)} = \frac{(6.62 \times 10^{-34})^2}{8 \times 9 \times 10^{-31}}\left(\frac{3 \times 5.86 \times 10^{28}}{3.14}\right)^{2/3}$$

$$= 9 \times 10^{-19} \text{ joules} = 5.6 \text{ electron-volts}$$

This is the maximum energy. The average energy can be obtained as

$$\epsilon_{Average} = \frac{\int \epsilon\, dn_\epsilon}{\int dn_\epsilon} = \frac{\int_0^{\epsilon_m}\epsilon^{3/2}d\epsilon}{\int_0^{\epsilon_m}\epsilon^{\frac{1}{2}}d\epsilon} = \tfrac{3}{5}\epsilon_m,$$

using eqn. (*ii*). Indeed the average energy of an electron in the electron gas is very high even at 0°K.

Now comparing eqns. (*iv*) and (*v*), we have

$$\frac{3}{2(\epsilon_m)^{3/2}}\int_0^{\infty}\frac{\epsilon^{1/2}d\epsilon}{Ae^{\beta\epsilon_i}+1} = 1 \qquad \ldots (vii)$$

Since $d\epsilon = kTd(\epsilon/kT)$, this eqn. may be written as

$$\frac{3}{2}\left(\frac{kT}{\epsilon_m}\right)^{3/2}\int_0^{\infty}\frac{(\epsilon/kT)^{\frac{1}{2}}\, d(\epsilon/kT)}{Ae^{\epsilon_i/kT}+1} = 1 \qquad \ldots (viii)$$

An approximate value of the integrand may be obtained in the following way. Let us first assume $Ae^{\epsilon/kT} \ll 1$, when the denominator of the integrand is unity. On the other hand if ϵ/kT becomes larger and larger, the value of the integrand gradually becomes smaller and smaller and approaches zero. It would not be unreasonable if the upper limit of the integration be fixed at ($ln\, 1/A$). Any higher value will make the integrand too small. Then

$$\frac{3}{2}\left(\frac{kT}{\epsilon_m}\right)^{3/2}\int_0^{ln\,1/A}\frac{(\epsilon/kT)^{\frac{1}{2}}\,d(\epsilon/kT)}{Ae^{\epsilon/kT}+1} = 1$$

or $$\frac{3}{2}\left(\frac{kT}{\epsilon_m}\right)^{3/2}\cdot\frac{2}{3}\,[ln\,1/A]^{3/2} = 1$$

$$\therefore \qquad A = e^{-\epsilon_m/kT} \qquad \ldots (ix)$$

Substituting in eqn (*iii*), we have the desired distribution of energy,

$$\frac{dn_\epsilon}{d\epsilon} = \frac{\pi(8m)^{3/2}V}{2h^3}\cdot\frac{\epsilon^{\frac{1}{2}}}{(e^{(\epsilon-\epsilon_m)/kT}+1)} \qquad \ldots (x)$$

It is assumed that $\epsilon_m \gg \epsilon$, *i.e.*, the majority of the electrons have energies much less than that of the Fermi level.

It is obvious from this distribution equation that *at* 0°*K*,

(*i*) When $\epsilon_m > \epsilon$., the exponential term becomes $-\infty$,

hence $\frac{dn_\epsilon}{d\epsilon}$ varies as ϵ

(*ii*) When $\epsilon_m < \epsilon$, the exponential term becomes $+\infty$

and hence $\frac{dn_\epsilon}{d\epsilon} = 0$.

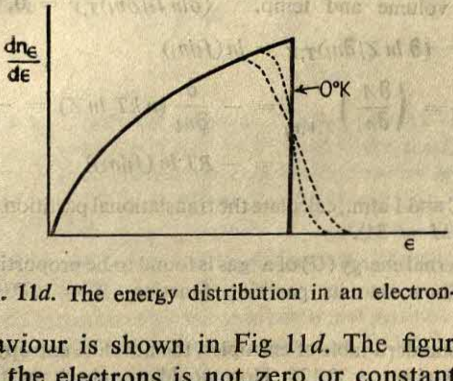

Fig. 11*d*. The energy distribution in an electron-gas.

This behaviour is shown in Fig 11*d*. The figure shows that the energy of the electrons is not zero or constant at 0°K. The maximum energy that of the Fermi level is indicated from the tip. If the temperature is raised, then a few electrons may pass on to a level slightly higher than the Fermi level. The curve would change a little as shown by the broken line.

Problems

1. Explain what is meant by 'molecular partition function, f'. Show that f/N is a dimensionless quantity.

2. Establish, from statistical considerations, $PV = RT$ for a mole of an ideal gas.

$$\left[\text{Hint :} \qquad P = NkT\left(\frac{\partial lnf}{\partial V}\right)_T = NkT\left[\frac{\partial(ln\phi V)}{\partial V}\right]_T\right.$$

$$\left.\text{when } \phi = f_{rot}\cdot f_{vib}\cdot\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

3. Estimate the entropy of CO gas at 1 atm and 27°C. Given moment of inertia, $I = 14.6\times10^{-40}$ gm. cm^2 ; symmetry number, $\sigma = 1$; wave number, $\omega = 2170$ cm^{-1} [Ans. $S_{300^\circ K} = 47.3$ cal/°K-mole]

4. Show that in an ideal gas mixture containing n molecules of the i th type,

$$\mu_i = -RT\,ln\,(f_i/n_i)$$

[Hint : Since $Z = f^N/(N_i\,!)$, hence for the ith type of molecules

$$Z = f_i^{n_i}/(n_i)\,! \qquad \text{or} \quad \ln Z = n_i\,ln f_i - ln\,(n!)$$

$$\text{or} \qquad \left(\frac{\partial lnZ}{\partial n_i}\right)_{T,V} = n_i\left(\frac{\partial ln\,f_i}{\partial n_i}\right)_{T,V} + ln\,f_i - ln\,n_i$$

At const. volume and temp. $(\partial ln\,f_i/\partial n_i)_{T,V} = 0$, hence

$$(\partial\,ln\,Z/\partial n_i)_{T,V} = ln\,(f_i/n_i)$$

$$\text{But} \quad \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = -\frac{\partial}{\partial n_i}(n\,kT\,ln\,Z) = -\,nkT\,ln\,\frac{f_i}{n_i}$$

$$= -\,RT\,ln\,(f_i/n_i)]$$

5. At 25°C and 1 atm., calculate the translational partition function of a mole of butadiene ($M = 54$). Ans. 9.4×10^{30}

6. The internal energy (U) of a gas is found to be proportional to its absolute temperature. Show that its partition function, $Z = AT^{c/R}$ where A and C are constants.

7. In the standard table of entropies, the absolute entropy of He (T=298°K, P = 1 atm.) is given as 30.126. How would you check up its correctness?

8. Show that at very high temperatures, the ratio of vibrational partition function to temperature (f_{vib}/T) of a given diatomic molecule is a constant. Also show that the ratio is inversely proportional to the fundamental frequency of vibration.

9. The normal vibration of H_2O molecule in wave number is 1595 cm^{-1}. Show that at 500°K one per cent of the molecules shall be in the first excited vibrational energy level.

10. For Nitrogen, the fundamental vibration in wave number is found to be 2360 cm^{-1}. Calculate the enthalpy function $(H_T{}^0-H_0{}^0)/T$ for the gas at 1000°C.

Ans. 7.188 cal/mole-deg.

[**Hint.** $(H_T{}^0-H_0{}^0)/T = U/T + R$, for $H_0{}^0 = 0$

Then show $U/T = kT \dfrac{\partial}{\partial T} \ln Z$

$$= RT \frac{\partial}{\partial T} \ln \left[(2\pi mkT/h^2)^{3/2} \left(\frac{Ve}{N} \right) . \tfrac{1}{2} . \frac{8\pi^2 IkT}{h^2} . \frac{e^{-h\nu_0/2kT}}{(1-e^{-h\nu_0/kT})} \right]$$

$$= (5/2)\, R + \frac{Nh\nu_0}{T} \left(\tfrac{1}{2} + \frac{1}{e^{-h\nu_0/kT}-1} \right)$$

Next proceed to evaluate.]

11. The frequency of absorption band for CO associated with its vibrational transition is 6.51×10^{13} per second.

(*i*) At what temperature does kT become equal to the energy of this vibrational transition?

(*ii*) Calculate the fraction of CO molecules in the vibrational level $v = 1$ at 27°C.

Now $e = h\nu = 6.63 \times 10^{-34}\,(J\text{-}s) \times 6.51 \times 10^{13}\, s^{-1} = 4.32 \times 10^{-20} J$

Hence, the temperature where $kT = \epsilon$, is $(k = 1.38 \times 10^{-23} J)$

$$T = \epsilon/k = 4.32 \times 10^{-20}/1.38 \times 10^{-23} = 3.12 \times 10^{3}\ {}^\circ K$$

Also, $\epsilon/kT = 4.32 \times 10^{-20}/(1.38 \times 10^{-23})\,(300) = 10.4$

Therefore
$$\frac{N_1}{N} = \frac{e^{-\epsilon_1/kT}}{\Sigma e^{-\epsilon_1/kT}} = \frac{e^{-10.4}}{e^{\frac{-0}{kT}} + e^{-10.4} + \ldots}$$

$$= e^{-10.4} \quad = 2.9 \times 10^{-6}$$

12. CO has an absorption band at 1400 Å due to electronic transition. Calculate the temperature at which kT is equal to the energy of the transition. Also estimate the fraction of molecules in the first excited level at 27°C.

[Ans. $T = 1.03 \times 10^{4}$°K, $n_1/n = 7.9 \times 10^{-14}$]

13. Compute the translational entropy of a mole of a monatomic gas at 1 atm as a function of M and T from partition function. Evaluate the expression for argon at 27°C ($M = 40$).

14. Calculate the value of the classical rotational partition function for carbon monoxide at 20°C. The internuclear distance, $r = 1.1282$ Å ; the atomic masses are $C = 12.00390$, $O = 16.00000$.

$$\left[Hint : I = \mu r^2 = \frac{12.00390 \times 16.00000}{28.00390} \times \frac{1}{6 \times 10^{23}} \times 1.1282 \times 10^{-16}\right.$$

$$= 14.49 \times 10^{-40} \text{ g-cm}^2\text{/molecule}$$

$$\left. f_r = \frac{8\pi^2 IkT}{h^2} \right]$$ **[Ans. 7.11940]**

15. Discuss the attempts which have been made to account quantitatively for the variation of atomic heat of solids with temperature.

16. Estimate the translational entropy of gaseous iodine at 25°C and 1 atm.

Now :

$$m = 2 \times 127 \times (1.66 \times 10^{-27} \text{ kg}) = 421.4 \text{ kg}$$

$$1 \text{ atm} = 1.01 \times 10^5 \text{ Nm}^{-2};\ T = 298°\text{K}$$

$$\therefore \frac{2\pi mkT}{h^2} = 2.48 \times 10^{22} \text{ m}^{-2}$$

Hence, $S = (8.32 \text{ JK}^{-1}) \, ln \, [e^{5/2}. \, (2.48 \times 10^{22} \text{m}^{-2})^{3/2} RT/P)]$

$$= 8.32(\text{JK}^{-1}) ln \, (1.94 \times 10^9) \approx 178 \text{ JK}^{-1} \text{ mol}^{-1}$$

17. Calculate the Fermi energy for Copper. Assume 1 free electron per atom. **[Ans. 7.07 ev]**

18. The heat-capacity of Aluminium per g-atom is 4.525 cal at 173°K. Compute the characteristic Debye temperature. **[Ans. 417°K]**

CHAPTER 12

THERMODYNAMICS & RADIATIONS

In the preceding chapters, the basic principles of thermodynamics and some important relations derived therefrom have been discussed. This chapter and those which would follow will be devoted to the application of the thermodynamic principles to common physical and chemical phenomena. The thermodynamic principles have been very aptly employed to the study of energy radiation, as will be shown in the following sections.

12.1. Radiation Pressure

Electromagnetic radiations are emitted by each body. It is now known that the radiations are atomistic in character and they are emitted or absorbed as energy quanta $h\nu$, where ν is the frequency of the radiation. These quanta of energy are called *photons* and an assembly of photons is termed the *photon gas*.

When radiations are incident on a body, there may be reflection, transmission and absorption of the radiations by the body. A black body is one which absorbs the entire radiation without any reflection or transmission. A perfectly black body must absorb totally the whole range of wavelengths of radiation. It must also emit radiation of the same character and intensity that which it absorbs. Lampblack or Platinum black will be the nearst approach to a blackbody. Any closed chamber, say a hollow sphere having a small opening at one point, is a perfect absorber, whatever the colour inside may be. The rays which enter the hole are repeatedly reflected from the walls of the hollow body and will ultimately be absorbed. The enclosure thus behaves as a black body in absorption and emission. The aperture of a hallow body will radiate as a perfect black body, say, at a temperature T. The emitted radiations are the same as those present inside the cavity. It would be our problem to find the distribution of the radiations among the various frequencies. Before solving this problem, it is necessary to know if the radiation has a pressure like a gas with which it is often compared.

Let us consider a cylindrical cavity inside which a portion (say, the bottom) is perfectly black which continuously emits and absorbs radiations of all frequencies. The walls of the cavity are perfectly reflecting. The cylinder is fitted with a frictionless movable piston. A quantity of energy U is always present in the system at temperature T. The system may be compared with a gas filling the space. There is one difference that energy density ρ ($= U/V$) depends only on the temperature T, where as the density of gas is changed with change in volume as well. If the piston is moved out (T, constant) more photons would be emitted keeping number of photons per unit volume constant. But in the case of a gas, the number of molecules per unit volume diminishes as the volume is expanded.

Now imagine a photon of frequency ν, hence energy $h\nu$, is present in a cubic vessel with perfectly reflecting walls of a cm length in each side. Since $h\nu = mc^2$, hence the mass of the proton $= h\nu/c^2$ and its momentum $h\nu/c$. If the photon moves perpendicularly to two of the opposite faces of the cube, it would be colliding with the walls and in each collision the change in momentum would be $2h\nu/c$ (as the velocity-direction is reversed).

Between two successive collisions on the same face, the time that elapses is $2a/c$; hence the number of collisions per second on the same face would be $c/2a$. Hence, the net change of momentum suffered by the photon for collisions on one face per second is

$$\frac{2h\nu}{c} \times \frac{c}{2a} = \frac{h\nu}{a}$$

Suppose there are N photons present in the cube, which are moving in all possible directions. On an average it may be presumed that $\frac{1}{3}$ of the photons are moving along x-axis (say). Hence, the change of momentum suffered by all photons at one face per second

$$= \frac{Nh\nu}{3a}$$

∴ The rate of change of momentum which is the impressed force,

$$F = \frac{Nh\nu}{3a}$$

The force per unit area (1 cm^2) *i.e.* the pressure

$$P_\nu = \frac{Nh\nu}{3a.a^2} = \frac{Nh\nu}{3a^3} = \frac{Nh\nu}{3V}.$$

Since the number of molecules per cm^3 is N/V, $= n$(say), so

$$P_\nu = \frac{nh\nu}{3}$$

But $nh\nu$ is the energy density (ρ). Therefore

$$P_\nu = \tfrac{1}{3}\rho_\nu \qquad \ldots (12.1)$$

This is true for every frequency ν. Hence, the total radiation pressure,

$$P = \Sigma\tfrac{1}{3}\rho_\nu = \tfrac{1}{3}\rho \qquad \ldots (12.2)$$

The quantity $\rho/3$ represents the mechanical pressure exerted on a reflecting surface by the 'photon gas' in equilibrium with the enclosed vessel. It should be remembered that for the radiations in an enclosure the energy density depends upon the temperature of the walls and is independent of the volume. If the volume expands at a constant temperature, more radiation is emitted, so that ρ (energy density) remains unaltered.

Experiments to prove the existence of radiation pressure have been made by Lebedew, by Nichols and Hull and by others.*

It will be useful to calculate also the energy emitted per second per unit area of any black surface. Let there be altogether n beams and let the energy density due to any one of them be ρ'. Half of the n beams are moving towards a given surface and each of them delivers energy $c\rho'\cos\theta$. The total energy brought up to the unit area per sec. is

$$\frac{n}{2}\int_0^{\pi/2} c\rho'\cos\theta\sin\theta\, d\theta = \tfrac{1}{4}c\rho' n = \tfrac{1}{4}c\rho$$

where ρ as usual, is the net energy density of the enclosure.

In an isothermal enclosure equal amount of energy is carried away from the surface. Again the stream of radiation that travels in one direction in an isothermal enclosure is the same as the stream of radiation emitted by any black surface at the same temperature. Hence, the energy emitted by a black body per unit area of its surface, *i.e.*, its emissive power is given by

$$E = \tfrac{1}{4}c\rho. \qquad \ldots (12.3)$$

i.e., E is proportional to ρ.

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* Phys. Rev. 13, 1901 ; Phys. Rev. May 1905; Jour. Asiatic. Soc. 14, 1918.

12.2. Stefan-Boltzmann law

In 1879, Stefan showed empirically from experimental results that the rate of emission of radiant energy from a black-body is proportional to the fourth power of the Kelvin temperature. In 1884, Boltzmann showed it to be a consequence of the application of thermodynamics.

Imagine a small enclosure of volume V, traversed by radiant energy. The radiation having a definite velocity, the enclosure will have a definite amount of energy, U. Then we have, $U = \rho V$ where ρ is the energy density of the radiation.

If the enclosure containing the radiation be placed in a heat reservoir at the same temperature T and then the volume is increased or decreased, there will be heat-flow from or to the reservoir. It is thus a case parallel to expansion or contraction of a gas in a cylinder under similar conditions. This enclosure has also the three paramenters P, V and T and the total radiant energy is U. We can now apply energy equation to this system.

$$\left(\frac{dU}{dV}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Since $U = \rho V$, and $P = \frac{1}{3}\rho$, we have

$$\rho = \frac{T}{3}\cdot\frac{d\rho}{dT} - \frac{\rho}{3}, \text{ or } \frac{d\rho}{\rho} = 4\frac{dT}{T}$$

or $\rho = aT^4$, where a is constant. . . . (12.4)

Now, the emissive power of a black surface,

$$E = \tfrac{1}{4}c\rho = \tfrac{1}{4}caT^4 = \sigma T^4 \qquad \text{. . . (12.5)}$$

where the constant σ $(= \frac{1}{4}ca)$, is called the Stefan's constant.

Thus we see that the energy density of radiation within an enclosure and the total emissive power of a black body are proportional to the fourth power of the absolute temperature T. This is generally known as the Stefan-Boltzmann Law.

The experimental verification of this law has been made by a number of investigators such as Lummer & Pringsheim, Mussmann, Muller, Hoare and others.*

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* See : Ann. d. physik 50, 259, 1916 ; Zeit f. physiq : 14, 315, 1923. Phil. mag. 6, 828, 1928 ; 13, 380, 1932. Phys. Rev., 34, 502, 1929.

The value of the Stefan constant has been found to be

$$\sigma = 5.67\times10^{-5} \text{ ergs per sec per } cm^{2}{}^{\circ}\text{K}^{-4}$$

Some more informations are also available.

(*i*) Supposing the photon gas has an entropy S, then

$$TdS = dU + PdV = d(\rho V) + \tfrac{1}{3}\rho dV$$

$$= Vd\rho + \rho dV + \tfrac{1}{3}\rho dV$$

or $$dS = \frac{V}{T}\left(\frac{\partial \rho}{\partial T}\right)_V dT + \tfrac{4}{3}\rho dV$$

or, $$dS = 4aT^2VdT + \tfrac{4}{3}aT^3dV \quad \text{(from eqn 12.4).}$$

$$\therefore \quad \left(\frac{\partial S}{\partial V}\right)_T = \tfrac{4}{3}aT^3 \qquad \text{. . . (12.6)}$$

That is, at a volume V, $S = \tfrac{4}{3}aVT^3$ . . . (12.7)

It means that the energy per unit volume is proportional to the fourth power of the temperature (°K) and the entropy per unit volume is proportional to the cube of the temperature.

(*ii*) If the enclosure containing the radiation be imagined to undergo an adiabatic expansion, we have

$$dU + PdV = dQ = 0$$

or $$d(\rho V) + \frac{\rho}{3}\, dV = 0$$

i.e., $$\rho dV + Vd\rho + \frac{\rho}{3}\, dV = 0$$

or $$\frac{4}{3}\frac{dV}{V} + \frac{d\rho}{\rho} = 0$$

or $$\ln \rho V^{4/3} = \text{constant}, \; i.e., \; \rho . V^{4/3} = k_1 \qquad \text{. . . (12.8)}$$

Hence, $$aT^4 . V^{4/3} = k_1$$

or $$VT^3 = \text{constant} \qquad \text{. . . (12.9)}$$

This relation is useful in the study of spectral distribution of energy.

12.3. Spectral distribution of radiation energy : Wien's Law

The Stefan-Boltzmann Law gives the relation between temperature and the total energy of the black-body radiation, but this does not indicate the distribution of energy in the different parts of the spectrum. The first notable success in this direction was achieved by Wien with his application of thermodynamical principles. Wien's treatment may be broadly considered in the following way:

(*a*) Imagine a spherical enclosure having perfectly (but diffusely) reflecting walls. The walls are elastic and by moving them outwards, the enclosed volume may be expanded. The enclosure is filled up with black-body radiations at temperature T. This is achieved by introducing a minute carbon-particle (at T abs.) and the radiation inside comes into equilibrium with the black-body. The carbon is subsequently removed.

(*b*) The enclosure is then expanded adiabatically by slowly moving the walls onwards with an uniform velocity v, such that $v \leqslant c$, the velocity of radiation. The volume increases by the amount $\triangle V$ and the temperature is lowered to T', such that $T-T' = \triangle T$. Although the temperature falls, the nature and quality of radiation will not change and will correspond to the full black radiation characteristic of temperature T'. This can be easily established thermodynamically.

Suppose the radiation in the enclosure after expansion does not correspond to that of full black radiation at T'. Let us also suppose that the radiation of frequency ν_1 is more preponderant and the radiation of frequency ν_2 is less compared to those of full black radiations at T'. Introduce now two small bodies A and B which absorb radiations of frequencies ν_1 and ν_2 respectively. 'A will be more heated than B. With the assistance of a Carnot engine working between A and B let us convert the excess heat in A into work until the nature of the radiations in the enclosure attains the quality of full black radiations. Due to the removal of a portion of energy as work, the temperature will diminish, say to T''. The system may then be adiabatically compressed to its original volume. The temperature will now be less than T, for some energy has already been taken away from the system. Moreover, according to our assumption the system will not have the quality of full radiation. We can therefore again insert a Carnot engine and obtain work to bring the system at full black radiations at a still lower temperature. Thus we shall be continuously producing work from a single body (the enclosure) by lowering its temperature without maintaining a sink. This is against the Second Law. The assumptions made are therefore wrong. The radiations in the enclosure are therefore full black radiations as of the lower temperature T'.

(*c*) We can now consider the effect due to expansion of the enclosure. The radiations are all moving with a velocity c and are incident on the walls. But the walls themselves are receding away with a velocity v. As a result there will be the Doppler effect. In consequence, the frequency of any particular wave will undergo a change. The new frequency will be, when the rays are normally incident,

$$\nu' = \nu\left(1 - \frac{v}{c}\right)$$

After reflection the frequency will again change in the same way. Thus the final frequency is given by, after a reflection,

$$\nu'' = \nu'\left(1 - \frac{v}{c}\right) = \nu\left(1 - \frac{v}{c}\right)^2 \approx \nu\left(1 - \frac{2v}{c}\right), \text{(since } v \ll c\text{)}$$

$$\therefore \triangle\nu = -\frac{2v}{c}\nu$$

$$\text{or} \quad \frac{d\nu}{\nu} = -\frac{2v}{c}; \quad i.e., \frac{\partial\lambda}{\lambda} = \frac{2v}{c} \ldots \text{(since } c = \nu\lambda\text{)}$$

The waves in the enclosure may be incident at any angle θ, so that velocity v will be effectively $v\cos\theta$; hence

$$\frac{d\lambda}{\lambda} = \frac{2v\cos\theta}{c}$$

The enclosure is spherical, the waves will reflect successively after travelling the distance given by a chord *AB* of the circle (Fig. 12*a*). The distance *BA* is thus $2r\cos\theta$. Hence the no. of collisions per second is $\frac{c}{2r\cos\theta}$

Hence, the total change in wavelength per unit time is

$$d\lambda = \frac{2v\cos\theta}{c} \cdot \frac{c}{2r\cos\theta}\lambda = \frac{v\lambda}{r}$$

$$\text{or} \quad \frac{d\lambda}{\lambda} = \frac{v}{r} = \frac{dr}{r}$$

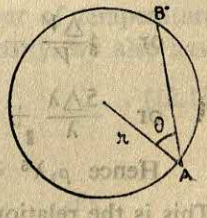

Fig. 12*a*

(where *dr* is the distance through which the walls move in unit time, *i.e.*, the velocity v of the walls).

(*d*) But we have seen, $\rho . V^{4/3} =$ constant [eqn. (12.8)] and $V = \frac{4}{3}\pi r^3$; $\rho = aT^4$ (Stefan-Boltzmann).
Substituting,

$$\rho V^{4/3} = aT^4\left(\tfrac{4}{3}\pi r^3\right)^{4/3} = k' r^4 T^4$$

$$\text{Hence} \qquad rT = \text{constant.}$$

or $$rdT + Tdr = 0$$

i.e., $$\frac{dr}{r} = -\frac{dT}{T}$$

Hence, equation (*i*) may be written as

$$\frac{\partial\lambda}{\lambda} = \frac{dr}{r} = -\frac{dT}{T}$$

i.e., $$\lambda T = \text{constant} = \lambda' T' \qquad \ldots (12.10)$$

The temperature varies inversely as the wavelength during the adiabatic changes of radiations.

(*e*) Let us now restrict ourselves only to the radiation having wavelengths between λ and $\lambda + \triangle\lambda$ suffering adiabatic expansion.

The work done during expansion $= (\frac{1}{3}\rho_\lambda d\lambda)\triangle V$

The decrease in energy $= -\triangle[V.\rho_\lambda d\lambda]$

and these two shall be equal.

$$\tfrac{1}{3}\rho_\lambda d\lambda \triangle V = -\triangle(V.\rho_\lambda d\lambda)$$

$$= -\triangle V\rho_\lambda d\lambda - V\triangle\rho_\lambda d\lambda - V\rho_\lambda\triangle(d\lambda)$$

or $$\tfrac{1}{3}\frac{\triangle V}{V} = -\frac{\triangle V}{V} - \frac{\triangle\rho_\lambda}{\rho_\lambda} - \frac{\triangle(d\lambda)}{d\lambda}$$

or $$\tfrac{4}{3}\frac{\triangle V}{V} = -\frac{\triangle\rho_\lambda}{\rho_\lambda} - \frac{\triangle\lambda}{\lambda} \text{ (since } \triangle\lambda \text{ changes in the same way as } \lambda)$$

or $$\tfrac{4}{3}\frac{\triangle V}{V} + \frac{\triangle\rho_\lambda}{\rho} + \frac{\triangle\lambda}{\lambda} = 0$$

or $$\frac{5\triangle\lambda}{\lambda} + \frac{\triangle\rho_\lambda}{\rho_\lambda} = 0^* \qquad [\text{Since } V \propto \lambda^3 \text{ ; see footnote}]$$

Hence $\rho_\lambda\lambda^5 = \text{constant} = \rho_\lambda'\lambda'^5$

This is the relation between energy density and wavelength of the radiation during adiabatic expansion. λ changes with temperature,

---

* We have $\lambda T = \text{const.}$ and $aT^4 = \rho$. Hence, $\lambda\rho^{\frac{1}{4}} = \text{const.}$

Again $\rho.V^{\frac{4}{3}} = \text{const.}$ or $\rho^{\frac{1}{4}} = V^{-\frac{1}{3}}$ . . . eqn. (12.8)

Hence $\lambda V^{-\frac{1}{3}} = \text{const.}$ *i.e.*, $V \propto \lambda^3$

i.e. $\ln V = 3 \ln \lambda$ or $\dfrac{\triangle V}{V} = 3\dfrac{\triangle\lambda}{\lambda}$

ρ_λ therefore must also depend on temperature. But ρ_λ changes in a way such that $\rho_\lambda \lambda^5$ is constant, and at the same time λ changes such that λT is constant. Hence $\rho_\lambda \lambda^5$ must be a function of (λT).

So, $$\rho_\lambda \lambda^5 = Af(\lambda T)$$

or $$\rho_\lambda d\lambda = \frac{A}{\lambda^5} f(\lambda T) d\lambda \qquad \ldots (12.11)$$

This is the Wien's displacement Law, which can also be expressed in terms of frequency, ν.

Since $$\lambda = \frac{c}{\nu}\,;\; d\lambda = -\frac{c}{\nu^2} d\nu$$

Then, $$\rho_\nu \left(\frac{-c}{\nu^2}\right) d\nu = \frac{A\nu^5}{c^5} f\left(\frac{cT}{\nu}\right)\left(\frac{-c}{\nu^2}\right) d\nu$$

or $$\rho_\nu d\nu = B\nu^3 f\left(\frac{\nu}{T}\right) d\nu \qquad \ldots (12.12)$$

Wien's Law will then give us the curve relating ρ_λ and λ for any temperature, when the curve for another given temperature is experimentally known.

Wien's equation (12.11) may also be written as,

$$\rho_\lambda d\lambda = \frac{AT^5}{(\lambda T)^5} f(\lambda T) d\lambda = AT^5 F(\lambda T) d\lambda$$

$$\left[\text{where } F(\lambda T) = \frac{f(\lambda T)}{(\lambda T)^5}\right]$$

For temp. T', $\rho_\lambda' d\lambda = AT'^5\, F(\lambda' T') d\lambda$

Hence $$\frac{\rho_\lambda}{\rho_\lambda'} = \left(\frac{T}{T'}\right)^5$$

The radiation density increases as the fifth power of temperature. As the emission is proportional to radiation density, we also have

$$\frac{E_\lambda}{E_\lambda'} = \left(\frac{T}{T'}\right)^5 \qquad \ldots (12.13)$$

The curve obtained by plotting the experimentally determined values of E against λ at a given temperature, T, has the form as shown in Fig. 12b in which there is a maximum. The curve for another higher temperature T' can be plotted in such way that each λ is reduced by the ratio $\left(\frac{T}{T'}\right)$ (so that λT remains constant) and E_λ

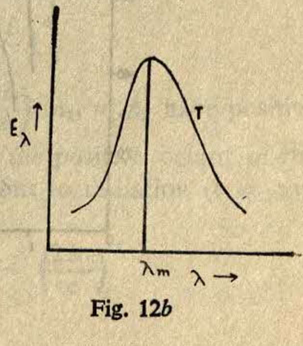

Fig. 12b

is increased by the ratio $\left(\frac{T'}{T}\right)^5$. If λ_m be the wavelength corresponding to a maximum, then

$$\lambda_m T = \text{constant } (b) = \lambda'_m T'$$

$$\text{and} \qquad E_m = \text{constant. } T^5 \qquad \ldots (12.14)$$

Wien's displacement Law was subjected to experimental tests. In Fig. 12*c* are given broadly the $E_\lambda - \lambda$ curves obtained by Lummer & Pringsheim for different temperatures. The radiations emitted from heated carbon tube was dispersed by a fluorspar prism and the distribution of energy measured with the help of a bolometer. Various necessary corrections were of course applied. The wavelengths were plotted in microns (10^{-4} cm) as abscissa and E_λ as ordinate. The curve corresponding to a higher temperature being always above that at the lower temperature.

It was found that Wien's Law is quite satisfactory when applied to short waves, but it does not conform to the experimental results for long waves and high temperatures.

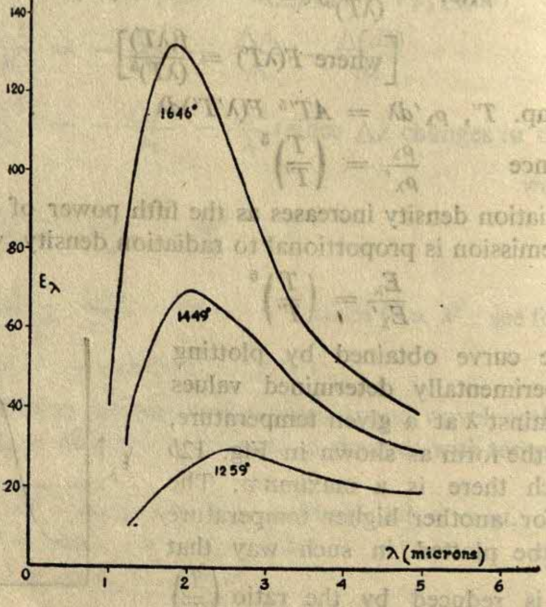

Fig. 12*c*

12.4. Raleigh-Jeans distribution law

Lord Raleigh attacked the problem from a different angle, which was ultimately given the complete form by Jeans. This treatment is based on the application of the principle of equipartition of energy for all the degrees of freedom which might be assigned to radiation.

When a string of length L, fixed at both ends, is subjected to vibration the standing waves can have only certain definite values of wave-length λ, represented by the relation, $\lambda = \frac{2L}{n}$, where n is an integer.

Instead of a string, we consider now a two dimensional vibrator, say a square with sides of length L. Let n_1, n_2 be the modes of vibration along two sides of the square at right angles when the steady state of vibration is reached. Both n_1 and n_2 shall have integral values. If the waves are at angle θ_1, to one side and θ_2 to the other (Fig. 12*d*), then,

$${}_1 = \frac{2L\ \mathrm{Cos}\theta_1}{\lambda},\ n_2 = \frac{L\ \mathrm{Cos}\theta_2}{\lambda};\ \text{and } \mathrm{Cos}^2\theta_1 + \mathrm{Cos}^2\theta_2 = 1$$

Similarly, for a three dimensional vibrator, say a cube with each side of length L, let n_1, n_2, n_3 be the respective modes of vibration along the three sides at right angles to one another, when steady state is attained. Assume also that θ_1, θ_2, θ_3 are the angles made by the waves with the three sides. Then we have,

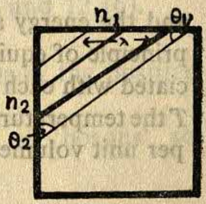

Fig. 12*d*

$$n_1 = \frac{2L\ \mathrm{Cos}\theta_1}{\lambda},\quad n_2 = \frac{2L\ \mathrm{Cos}\theta_2}{\lambda},\quad n_3 = \frac{2L\ \mathrm{Cos}\theta_3}{\lambda}$$

and $\quad \mathrm{Cos}^2\theta_1 + \mathrm{Cos}^2\theta_2 + \mathrm{Cos}^2\theta_3 = 1$

Hence $\quad n_1^2 + n_2^2 + n_3^2 = \left(\frac{2L}{\lambda}\right)^2$

This indicates a sphere of radius $\left(\frac{2L}{\lambda}\right)$, n_1, n_2, n_3 have positive integral values and must be located in the positive octant of the said sphere. Applying these considerations to radiation ($c = \nu\lambda$), we find

$$n_1^2 + n_2^2 + n_3^2 = \left(\frac{2L}{\lambda}\right)^2 = \left(\frac{2L\nu}{c}\right)^2$$

The possible modes of vibration of frequency lying between 0 and ν are given by the volume of the sphere of radius $\frac{2L\nu}{c}$

i.e. $$N = \tfrac{1}{8}\times\tfrac{4}{3}\pi\left(\frac{2L\nu}{c}\right)^3 = \tfrac{4}{3}\frac{\pi V}{c^3}\nu^3$$

The modes of vibration between ν and $\nu + \triangle\nu$ in the volume V will be

$$dN = \frac{4\pi V}{c^3}\nu^2 d\nu \qquad \ldots (12.15)$$

The modes of vibration per unit volume is $\frac{4\pi\nu^2}{c^3}\,d\nu$. Applying this idea in case of electromagnetic waves and remembering that these waves are independently polarised in two directions at right angles the number of vibrations will be double, *i.e.*,

$$dN = \frac{8\pi}{c^3}\nu^2 d\nu \qquad \ldots (12.16)$$

Now for every vibration, there are two degrees of freedom and the energy associated with each degree of freedom, from the principle of equipartition of energy is $\frac{1}{2}kT$. Hence the energy associated with each mode of vibration is kT, (k, Boltzmann constant ; T the temperature of the radiation). So, the total energy of radiation per unit volume is

$$kT\frac{8\pi}{c^3}\nu^2 d\nu$$

This is the same as the energy density of radiation between ν and $\nu + \triangle\nu$; or

$$\rho_\nu d\nu = kT\frac{8\pi\nu^2}{c^3}d\nu \qquad \ldots (12.17)$$

i.e., $$\rho_\lambda d\lambda = kT8\pi\lambda^{-4}\,d\lambda \qquad \ldots (12.18)$$

This is Raleigh-Jeans Equation.

When compared with the experimental observations, Raleigh-Jeans law is found to hold good for smaller frequencies but fails in case of larger frequencies. It is just opposite to that of Wien, which is valid for larger frequencies only. So none of the two relations are applicable through the entire spectral distribution. Moreover, eqn. (12.17) shows that the radiation intensity should increase continuously with increasing frequency, ν, at any given temperature. This is in complete disagreement with the experimental results, where the radiation-intensity rises to a maximum and then falls sharply with increase in frequency. Raleigh-Jeans Law, which is deduced from classical mechanics therefore fails. A solution to the problem was ultimately achieved by Max Planck (1900).

12.5. Planck's Distribution Law

It was Planck who finally produced the most satisfactory expression representing the energy distribution amongst the different frequencies at a given temperature. To determine the energy distribution, it is necessary to ascertain the number of photons having frequencies between ν and $\nu + d\nu$. Considering photon as a standing wave, we have seen in the previous section (12-4) that the number of standing waves dg_i with frequencies between ν and $\nu + d\nu$ in volume V is given by

$$dg_i = \frac{8\pi V}{c^3}\nu^2 d\nu \qquad \text{(see eqns. 12.15 and 12.16).}$$

This corresponds to the number of points which lie in the positive octant of a spherical shell of radius ν and $\nu + d\nu$.

The photons have been assumed to behave as 'bosons', so according to the Bose-Einstein distribution law,

$$n_i = \frac{g_i}{e^{h\nu/kT} - 1}$$

or

$$dn_i = \frac{1}{e^{h\nu/kT} - 1} dg_i \qquad \ldots (12.19)$$

Substituting the value of dg_i,

$$dn_i = \frac{8\pi V\nu^2}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} d\nu \qquad \ldots (12.20)$$

The energy of a photon is $h\nu$; the total radiation energy between the interval ν and $\nu + d\nu$, would be $h\nu dn_i$.

$\therefore$ Energy density in the given frequency interval is

$$\frac{h\nu dn_i}{V} = \rho_\nu' d\nu \qquad \ldots (12.21)$$

Combining eqns. (12.20 and 12.21),

$$\rho_\nu' = \frac{8\pi\nu^3 h}{c^3}\,\frac{1}{e^{h\nu/kT}-1} \qquad \ldots (12.22)$$

Most often, the energy-density is expressed in terms of wave-length (λ) instead of frequency (ν),

$$\nu = c/\lambda \qquad \text{or} \qquad d\nu = -(c/\lambda^2)d\lambda$$

By transformation, $$\rho_\lambda' = \frac{8\pi hc\lambda^{-5}}{e^{hc/\lambda kT}-1} \qquad \ldots (12.23)$$

This is the famous Planck's energy distribution law. The experimental measurments have fully confirmed this relation (see fig. 12*e*). The validity of this equation justifies the assumption that photons would obey *B-E* statistics.

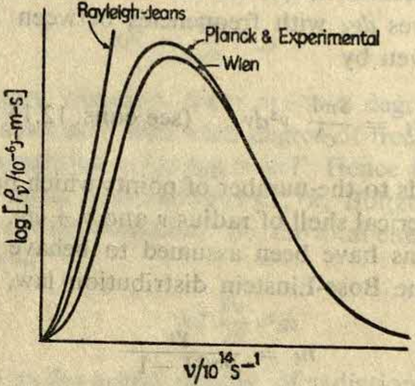

Fig. 12*e*

The average value of ρ (the energy density) is obtained if the energy-density (eqn. 12.23) be integrated per unit wave-length for values from 0 to ∞.

$$\rho' = \int_0^\infty \rho_\lambda' d\lambda = 8\pi hc \int_0^\infty \frac{1}{\lambda^5(e^{hc/\lambda kT}-1)}\,d\lambda$$

Putting $hc/\lambda kT = Z$ and $B = hc/k$, the expression would be

$$\rho' = 8\pi hc\,\frac{T^4}{B^4}\int_0^\infty \frac{Z^3}{e^z-1}dZ$$

$$\text{But} \int_0^\infty \frac{Z^3}{e^z - 1}\, dZ = \frac{\pi^4}{15} \text{ hence}$$

$$\rho' = \frac{8\pi^5 (kT)^4}{15\, c^3 h^3} = aT^4 \qquad \ldots (12.24)$$

That is, Stefan-Boltzmann law is a consequence of the Planck's distribution law. And

$$a = \frac{8\pi^5 k^4}{15\, c^3 h^3} \qquad \ldots (12.25)$$

Putting the values of k, c and h, the constant a is found to be

$$a = 7.5 \times 10^{-15} \text{ dyne-cm/cm}^3\ (^\circ\text{K})^4$$

Notes : We may consider some special cases for equation (12.23).

(*i*) When frequency is very large , *i.e.* λ is very small, $ch/\lambda \gg kT$, then the Planck's equation would be

$$\rho_\lambda{}' = \frac{8\pi hc}{\lambda^5} e^{-ch/\lambda kT}$$

$$= A.\lambda^{-5} f_1(\lambda T),$$

which is indeed the Wien's Law.

(*ii*) When the frequency is very small, *i.e.*, λ is very large $ch/\lambda \ll kT$, the Planck's equation may be written as,

$$\rho_\lambda{}' = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{1 + \frac{hc}{\lambda kT} - 1}$$

$$= 8\pi kT\, \lambda^{-4}$$

This is the same as Raleigh-Jeans law.

Problems

1. How would you justify that Bose-Einstien statistics is applicable to 'photon gas'?

2. Deduce Stefan-Boltzmann relation from the Planck Distribution Law.

3. Estimate the entropy of black-body radiation at a temperature of 1000°K.

CHAPTER 13

CHANGES OF PHASE

The study of changes of phase of substances, such as vaporisation, fusion, etc. is primarily based on thermodynamic principles. We shall consider in this chapter the application of thermodynamic laws to different types of phase-changes.

13.1. Clapeyron Equation

There is a correlation between the pressure and the temperature at which a phase-change takes place. This relation can be derived as follows.

(*i*) Suppose a pure substance is present in a system in two phases A and B. Let the molar free energies in the two phases be $\bar{G}_A$ and $\bar{G}_B$. Then, at equilibrium, (eqn. 10.1),

$$\bar{G}_A = \bar{G}_B$$

If the temperature is changed by a small amount dT and the system adjusts itself to a new equilibrium by a small change of pressure dP, then for the new equilibrium state,

$$\bar{G}_A + d\bar{G}_A = \bar{G}_B + d\bar{G}_B$$

$$\therefore \quad d\bar{G}_A = d\bar{G}_B \qquad \ldots (13.1)$$

Since $dG = VdP - SdT$, we have for the two phases,

$$d\bar{G}_A = \bar{V}_A dP - \bar{S}_A dT \quad \text{and} \quad d\bar{G}_B = \bar{V}_B dP - \bar{S}_B dT$$

where $\bar{V}_A$, $\bar{V}_B$ are the molar volumes and $\bar{S}_A$, $\bar{S}_B$ are the molar entropies of the substance in the two phases. The equation 13.1 now transforms to

$$\bar{V}_A dP - \bar{S}_A dT = \bar{V}_B dP - \bar{S}_B dT$$

$$\text{or} \qquad \frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{\triangle S}{(V_B - V_A)}$$

$$\text{or} \qquad \frac{dP}{dT} = \frac{T \triangle S}{T(V_B - V_A)} = \frac{q}{T(V_B - V_A)}$$

The heat-change q in this case is the latent heat of the phase-change, i.e.,

$$\frac{dP}{dT}=\frac{L}{T(V_B-V_A)} \qquad \ldots (13.2)$$

where L = molar latent heat. This relation is applicable to any phase-change. V_B is the final and V_A is the initial volume. This relation can also be derived in other ways.

(*ii*) From Maxwell's relations, we have

$$\left(\frac{\partial P}{\partial T}\right)_V=\left(\frac{\partial S}{\partial V}\right)_T$$

When two phases are in equilibrium, say a solid and a liquid or a liquid and a vapour, the vapour pressure is independent of the mass and, hence, of the volume. Therefore, in such cases, we may write,

$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{dP}{dT}$$

Further, if we consider the latent heat of the change, L, as nearly constant and independent of temperature, we have

$$\left(\frac{\partial S}{\partial V}\right)_T=\frac{1}{T}\left(\frac{\partial Q}{\partial V}\right)_T=\frac{L}{T(V_B-V_A)}$$

Thus,
$$\frac{dP}{dT}=\frac{L}{T(V_B-V_A)}$$

As before : the same relation is obtained. This is called the *Clapeyron equation*.

The sign of $\frac{dP}{dT}$ depends on the signs of L and $\triangle V$. Thus, if L is positive and $V_B > V_A$, there would be a rise in pressure with increase in temperature. In the evaporation of a liquid these conditions prevail, and as such, the vapour pressure increases with rise in temperature. In the melting of a solid, L is positive and if $V_l > V_s$, melting temperature would increase with pressure as in the case of paraffin. But if $V_l < V_s$, higher pressure will lower the melting temperature, as in the case of ice.

This relation would also apply to the transformation of one modification of a solid to another, say α-sulphur to β-sulphur ; L would, of course, mean the heat of transformation.

13.2. Clausius-Clapeyron Equation

The Clapeyron-equation may be simplified in the case of vaporisation of a substance. In such a case, the relation is,

$$\frac{dP}{dT}=\frac{L}{T(V_g-V_l)}, \qquad (V_g = \text{volume of gas},\ V_l = \text{volume of liquid}).$$

Since $V_l \leqslant V_g$, so approximately,

$$\frac{dP}{dT}=\frac{L}{TV_g}=\frac{L}{T(RT/P)}=\frac{L.P}{RT^2}, \text{ (for one mole)}$$

assuming the vapour to behave as a perfect gas.

$$\therefore \qquad \frac{1}{P}\frac{dP}{dT}=\frac{L}{RT^2} \qquad \ldots (13.3)$$

or

$$\frac{d\,ln\,P}{dT}=\frac{L}{RT^2} \qquad \ldots (13.4)$$

where L is the latent heat per gm-mole.

If we further assume that the latent heat practically remains constant in the temperature range T_1 to T_2, the integration of this relation gives,

$$ln\,P=-\frac{L}{RT}+C_l \text{ (const.)} \qquad \ldots (13.5)$$

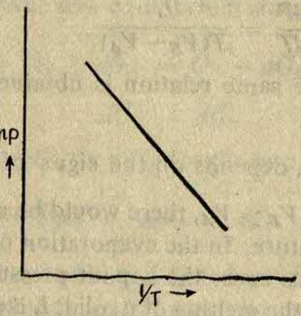

Fig. 13*a*

or

$$ln\,\frac{P_1}{P_2}=-\frac{L}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \qquad \ldots (13.6)$$

i.e.,

$$\log\frac{P_1}{P_2}=-\frac{L}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \qquad \ldots (13.7)$$

It is needless to mention that this relation is also applicable to sublimation processes where L would be the latent heat of sublimation.

The equations (13.3 ~ 13.7) are the different forms of Clausius Clapeyron-equations.

Problems : (*i*) Calculate the freezing temperature of water if the pressure be increased by one atmosphere. (Latent heat of fusion = 80 cal/gm)

Since $$\frac{\Delta P}{\Delta T} = \frac{L}{T(V_{\text{ice}} - V_{\text{water}})}$$

$$\therefore \quad \Delta T = \frac{\Delta P . T(V_{\text{ice}} - V_{\text{water}})}{L} = \frac{13.6 \times 981 \times 76 \times 273 \times .09}{-(80 \times 4.2 \times 10^7)} = -0.008°\text{C}$$

(*ii*) Calculate the specific volume of ether-vapour at its boiling point (35°C).

Given $L = 86$ cal/gm, $\frac{dP}{dT} = 27$ mm and density of liquid ether = 0.7 gm/c.c.

We know, $$\frac{dP}{dT} = \frac{L}{T(V_g - V_l)}$$

or $$2.7 \times 13.6 \times 981 = \frac{86 \times 4.2 \times 10^7}{\left(273 + 35\right)\left(V_g - \frac{1}{0.7}\right)}$$

whence, $V_{\text{gas}} = 322$ c.c.

i.e., the specific volume of ether vapour = 322 c.c.

(*iii*) Under what pressure will water boil at 98°C? (l = 536 cal/gm)
Using equation (13.3),

$$\Delta P = \frac{L . P}{RT^2} . \Delta T = \left[\frac{18 \times 536}{2 \times 373^2} \times 760 \times (-2)\right] \text{mm} = -54 \text{ mm}$$

Hence, water would boil at 98°C at 706 mm pressure.

(*iv*) The densities of α- and β-sulphur are 2.00 and 1.95 respectively at their transition temperature, 96°C. The transition temperature changes by 0.036° for every atmosphere rise in pressure. Find out the heat of transition.

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{T(V_\beta - V_\alpha)}$$

$$\text{or } \Delta H = \frac{\Delta P}{\Delta T} T(V_\beta - V_\alpha) = \frac{1}{0.036} \times (273 + 96)\left[\frac{1}{1.95} - \frac{1}{2.00}\right] \text{c.c.-atm.}$$

$$= 3.16 \text{ calories per gm}$$

13.3. Trouton's Rule. From equation (13.5), for the vaporisation of a liquid,

$$\ln P = -\frac{L}{RT} + C_1, \text{ (for 1 gm-mole)}$$

If we consider the liquids at their boiling temperatures T_b, then the pressure P will be one atmosphere (*i.e.*, $P = 1$).

or $$\frac{L}{T_b} = RC_1 = C \text{ (constant)}, \quad \ldots (13.8)$$

where L is the molar latent heat of vaporisation.

Trouton had made this important generalisation from experimental observations and stated that *the ratio of the molar heat of vaporisation to the boiling temperature is a constant for simple or non-associated liquids and the constant is approximately* 21. In other words, the molar entropy-change on vaporisation at the boiling temperature is constant. In Table A below are given the entropy-changes of vaporisation for some liquids at their boiling-temperatures.

TABLE A : MOLAR ENTROPY-CHANGES OF VAPORISATION

Substance	*B.Pt* (°C)	$\frac{L}{T_b}$	*Substance*	*B.Pt.* (°C)	$\frac{L}{T_b}$
n-Hexane	68.7	20.28	Hydrogen bromide	− 67	21.0
n-Heptane	98.4	20.61	Hydrogen fluoride	104	16.0
n-Octane	125.6	20.96	Oxygen	−183	18.0
Benzene	80.1	20.81	Nitrogen	−196	17.3
Toluene	110.6	20.85	Hydrogen	−257	15.61
o-Xylene	144.4	21.07	Water	100	28.7
m-Xylene	139.0	21.10	Ammonia	− 33	24.2
p-Xylene	138.4	20.95	Zinc	907	23.5
Carbon disulphide	46	21.0	Cadmium	767	22.9
Hydrogen chloride	−85	21.7	Mercury	357	22.4

It is observed that Trouton's Rule fails for liquids which are associated and also in the case of low-boiling or high-boiling liquids. Hildebrand modified Trouton's Rule and suggested that molar entropy-changes should be compared at temperatures when the vapours are in *equal concentrations* and not at unit atomosphere. Arbitrarily, the concentration chosen was 0.005 moles per litre, the entropy-change per mole, $\triangle S = \frac{L}{T_\epsilon}$, where T_ϵ is the temperature having the aforesaid concentration. Table B gives the values obtained on this basis.

TABLE B : ENTROPY-CHANGES (HILDEBRAND'S RULE)

Substance	$\triangle S = \frac{L}{T_\epsilon}$	*Substance*	$\triangle S = \frac{L}{T_\epsilon}$
Oxygen	27.6	Zinc	26.4
Nitrogen	27.6	Cadmium	26.4
Hexane	27.2	Mercury	26.2
Benzene	27.4		
Octane	27.6	Alcohol	32.0
Carbon tetrachloride	27.0	Water	32.0

A more satisfactory relation has been developed by Kistiakowsky (1923) in the form

$$\frac{\triangle H_n}{T_n} = 8.75 + R \ln T_n \quad \text{. . . (13.4)}$$

where $\triangle H_n$ is the latent heat of vaporisation of a liquid at its normal b. pt. T_n.

A useful empirical relation : van der Waals proposed a quite satisfactory empirical relation between vapour pressure P and temperature T, in the form,

$$\log \frac{P}{P_c} = k \left(1 - \frac{T_c}{T}\right) \quad \text{. . . (13.10)}$$

For many liquids, k is found to be approximately 3.0 and is taken as a universal constant.

If this relation be applied at the normal b. pt. T_b of a liquid, the vapour pressure is $P = 1$ atm.

Hence
$$\log \frac{1}{P_c} = k \left(1 - \frac{T_c}{T_b}\right)$$

or
$$\frac{T_b}{T_c} = \frac{k}{k + \log P_c}$$

For most substances, $\log P_c \approx 2$; hence taking $k = 3.0$,

$$\frac{T_b}{T_c} = 0.6$$

This is found to be valid for many substances.

13.4. Dependence of Vapour Pressure on total Pressure

The equilibrium between liquid and vapour is usually observed in presence of the atmosphere. It is interesting to find out whether the presence of air has any effect on the equilibrium vapour pressure.

Let P = total atmospheric pressure and p = partial pressure of the vapour in the gas phase above the liquid at equilibrium.

Since liquid and its vapour are in equilibrium at total pressure P and temperature T, then the molar free energy,

$$\bar{G}_{\text{gas}} = \bar{G}_{\text{liq}}$$

But the free energy at the gas phase at constant T and pressure p is given by

$$\bar{G}_{\text{gas}} = \bar{G}^{\circ}_{\text{ga}} + RT\,ln\,p$$

where $\bar{G}^{\circ}_{\text{gas}}$ is the standard free energy.

$$RT\,ln\,p = \bar{G}_{\text{liq}} - \bar{G}^{\circ}_{\text{gas}}$$

$$\therefore \quad R\,ln\,p = \frac{\bar{G}_{\text{liq}}}{T} - \frac{\bar{G}^{\circ}_{\text{gas}}}{T}$$

Differentiating this relation with respect to the total pressure P at a constant temperature,

$$R\left(\frac{\partial\,ln\,p}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial \bar{G}_{\text{liq}}}{\partial P}\right)_T \qquad \ldots (13.12)$$

as $\bar{G}^{\circ}_{\text{gas}}$ is constant.

Further, we know, $(\partial G/\partial P)_T = V$, hence equation (13.12) would be,

$$\left(\frac{\partial\,ln\,p}{\partial P}\right)_T = \frac{\bar{V}_{\text{liq}}}{RT}, \qquad \ldots (13.13)$$

$\bar{V}_{\text{liq}}$ is the molar volume of the liquid.

The change in vapour-pressure with the change in the total pressure (P) is usually very small.

13.5. Clausius Equation

So far the latent heat for the change of phase has been assumed to be constant in small ranges of temperature. But when the temperature-changes are large, the latent heat alters appreciably as shown in Fig. 13.*b*.

In a change of phase, if S_i and S_f denote the entropies in the initial and final states, then obviously $S_f - S_i = L/T$, where L is the latent heat of the process.

That is,

$$\frac{d}{dT}\left(\frac{L}{T}\right) = \frac{dS_f}{dT} - \frac{dS_i}{dT}$$

or $$\frac{1}{T}\frac{dL}{dT} - \frac{L}{T^2} = \frac{dS_f}{dT} - \frac{dS_i}{dT}$$

or $$\frac{dL}{dT} = \frac{L}{T} + \frac{TdS_f}{dT} - \frac{TdS_i}{dT}$$

If C_f and C_i be the heat-capacities in the final and initial states, *under saturated conditions, then,*

$$\frac{dL}{dT} = \frac{L}{T} + C_f - C_i \qquad \ldots (13.14)$$

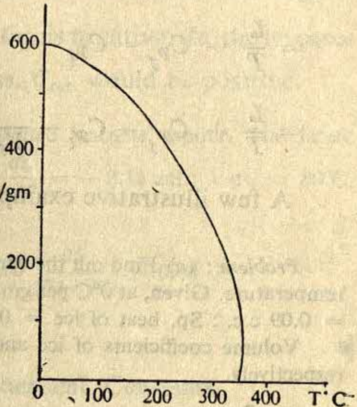

Fig. 13*b*. Variation of latent heat of vaporisation of water with temp.

This is known as the equation of Clausius and it gives us the variation of latent heat with temperature for any process involving a change of phase.

The equation can be modified also in the following fashion. We have, from the *TdS* equation (7.3),

$$TdS = dQ = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

or $$\left(\frac{T\partial S}{\partial T}\right)_{\text{sat}} = C_P - T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$$

The suffix 'sat' denotes equilibrium between two phases, in saturated states, such as the liquid and its saturated vapour phase.

Hence, $$C_{\text{sat}} = C_P - T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_{\text{sat}}$$

C_{sat}, denotes the heat capacity of the vapour in saturated state. Substituting this in equation (13.14),

$$\frac{\partial L}{\partial T} = \frac{L}{T} + C_{\text{sat}_f} - C_{\text{sat}_i}$$

$$= \frac{L}{T} + \left[C_{p_f} - T \left(\frac{\partial V_f}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{\text{sat}} \right]$$

$$- \left[C_{p_i} - T \left(\frac{\partial V_i}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_{\text{sat}} \right]$$

$$= \frac{L}{T} + C_{p_f} - C_{p_i} - T \left(\frac{\partial P}{\partial T} \right)_{\text{sat}} \left[\left(\frac{\partial V_f}{\partial T} \right)_P - \left(\frac{\partial V_i}{\partial T} \right)_P \right]$$

$$= \frac{L}{T} + C_{p_f} - C_{p_i} - \frac{L}{V_f - V_i} \left[\left(\frac{\partial V_f}{\partial T} \right)_P - \left(\frac{\partial V_i}{\partial T} \right)_P \right] \ldots (13.15)$$

A few illustrative examples may be taken.

Problem : (*a*) Find out the variation in the latent heat of fusion of ice with temperature. Given, at 0°C per gm. of the substance, $L = 80$ cal ; $V_{\text{ice}} - V_{\text{water}} = 0.09$ c.c. ; Sp. heat of ice = 0.505.

Volume coefficients of ice and water are 1×10^{-4} and -5×10^{-5} per °C respectively.

Since, $$\frac{\partial L}{\partial T} = \frac{L}{T} + C_{p_w} - C_{p_{ice}} - \frac{L}{V_w - V_{ice}} \left[\left(\frac{\partial V_w}{\partial T} \right)_P - \left(\frac{\partial V_{ice}}{\partial T} \right)_P \right]$$

$$= \frac{80}{273} + 1 - 0.505 + \frac{80}{0.09} \left[-5 \times 10^{-5} - 1 \times 10^{-4} \right]$$

$= 0.65$ cal per gm. per degree

(*b*) Heat-capacity of saturated water-vapour.

Calculate the heat-capacity of saturated water-vapour at 100°C. The latent heat of vaporisation = 540 cal/gm ; $\frac{\partial L}{\partial T} = -0.64$; and the heat capacity of water at 100°C = 1.01 cal/gm.

By equation (13.14),

$$C_{sat.vap.} = \frac{\partial L}{\partial T} - \frac{L}{T} + C_{water} = -0.64 - \frac{540}{373} + 1.01$$

$= -1.07$ cal. per gm. per °C.

The result is negative and may seem surprising. But this is quite possible. The heat capacity, $C = \frac{dU}{dT} + P\frac{dV}{dT}$

The first term is positive, but the second term would be negative when the vapour is to remain saturated. Suppose we have a quantity of saturated vapour to which heat is supplied to raise its temperature. Unless the vapour is compressed, the vapour would not remain in saturated state, i.e. dV is negative. The heat of compression exceeds the heat to be supplied and as such unless heat is removed, there would be superheating. In the cases of water-vapour, $P\frac{dV}{dT}$ is negative and greater than $\frac{dU}{dT}$, hence C_{sat} is negative. In those cases where the work of compression is less, C_{sat} would be positive.

(*c*) Calculate the heat-capacity of saturated benzene vapour. The latent heat of vaporisation = 95 calories per gm ; $\frac{dL}{dT} = -0.12$ cal.; b.pt. = 80°C, sp. heat of liquid = 0.48.

$$C_{\text{sat}} = \frac{\partial L}{\partial T} - \frac{L}{T} + C_l = -0.12 - \frac{95}{273+80} + 0.48$$

$$= +0.09 \text{ cal. per gm per °C.}$$

13.6. Vapour Pressure Equation : Chemical Constants

The vapour pressure of substances in the condensed state—solids or liquids—especially at low temperatures can be obtained with the help of the Clapeyron equation. At low temperatures the vapour pressures are quite small and are supposed to behave ideally. For vaporisation, the enthalpy change is really the latent heat of vaporisation. So, with the help of Kirchhoff's equation, we have,

$$L_T - L_0 = \triangle H_T - \triangle H_0 = \int_0^T \triangle C_P dT$$

or

$$L_T = L_0 + \int_0^T (C_{p_g} - C_{p_c})\, dT \qquad \ldots (13.16)$$

where C_{p_g} and C_{p_c} are the heat capacities of vapour and of condensed state.

Now, from Clapeyron equation,

$$\frac{d \ln P}{dT} = \frac{L_T}{RT^2} = \frac{L_0 + \int_0^T C_{p_g} dT - \int_0^T C_{p_c} dT}{RT^2}$$

Integrating,

$$\ln P = -\frac{L_0}{RT} + \int_0^T \frac{dT}{RT^2} \int_0^T C_{p_g} dT - \int_0^T \frac{dT}{RT^2} \int_0^T C_{p_c} dT + Z_1 \text{ (const.)}$$

$$\ldots (13.17)$$

Now, if we assume ideal behaviour for the vapour and if the vapour be monatomic (which is true in the case of metals especially), $C_{P_g} = (5/2)\,R$.

$$\therefore \qquad lnP = -\frac{L_0}{RT} + \tfrac{5}{2}\,ln\,T - \int_0^T \frac{dT}{RT^2}\int_0^T C_{P_c}\,dT + Z_1$$

or

$$lnP = -\frac{L_0}{RT} + \tfrac{5}{2}\,ln\,T + \frac{1}{RT}\int_0^T C_{P_c}\,dT - \int_0^T \frac{C_{P_c}}{RT}\,dT + Z_1$$

Expressing the pressure in atmospheres and converting into Briggsian logarithms,

$$\log_{10} P = -\frac{L_0}{2.303\,RT} + \tfrac{5}{2}\log_{10} T + \frac{1}{2.303\,RT}\int_0^T C_{P_c}\,dT$$

$$-\frac{1}{2.303\,RT}\int_0^T C_{P_c}\,d\,ln\,T + \frac{Z_1}{2.303} - \log\,(1.014 \times 10^6)$$

Putting $Z_1/2.303 - \log\,(1.014 \times 10^6) = i$ (constant).

$$\log_{10} P = -\frac{L_0}{2.303\,RT} + \tfrac{5}{2}\log_{10} T + \frac{1}{2.303\,RT}\int_0^T C_{P_c}\,dT$$

$$-\frac{1}{2.303\,R}\int_0^T C_{P_c}\,d\,ln\,T + i \qquad \ldots (13.18)$$

where i is called the *vapour-pressure constant* or *the chemical constant*. It shows that the knowledge of the chemical constant with some thermal data would enable us to calculate the vapour pressure of substances at very low temperatures. The chemical constant values of many substances have now been determined accurately.

This, of course, would require the knowledge of $\int_0^T C_{P_c}\,dT$ and $\int_0^T C_{P_c}\,d\,ln\,T$. Usually C_{P_c} is determined at different temperatures starting from the absolute zero (with necessary extrapolation) to the temperature as required. The C_{P_c}-values are plotted against T and the area under the curve up to T-axis gives the value of

$\int_0^T C_{P_c}\,dT$. Similarly, plotting C_{P_c} against $\log_{10} T$, the values of $\int_0^T C_{P_c}\,d\ln T$ are also found out. Now, from equation (13.18),

$$\log_{10}P-\tfrac{5}{2}\log T-\frac{1}{2.303\ RT}\int_0^T C_{P_c}\,dT+\frac{1}{2.303\ R}\int_0^T C_{P_c}\,d\ln T$$

$$=-\frac{L_0}{2.303\ RT}+i$$

Poltting the expression on the left-hand against $1/T$, a straight line is obtained, the intercept gives the value of i and the slope $=-L_0/2.303R$ (Fig. 13.3).

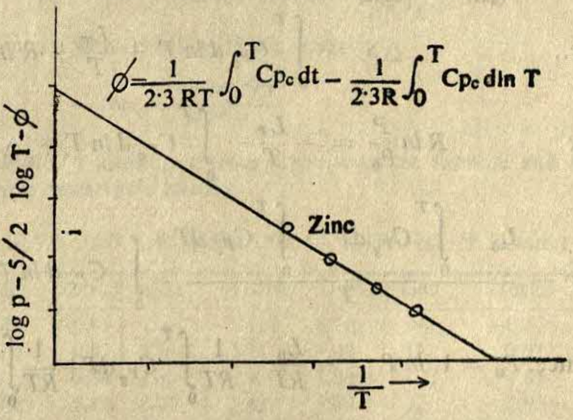

Fig. 13*c*. Determination of vapour-pressure constant

When a high degree of accuracy is not required, some empirical relations are often used to calculate the vapour pressure in place of equation (13.18), such as,

$$(i)\ \ln P = A-\frac{B}{T}+C\ln T\ \text{(Kirchhoff, Rankine, etc.)}$$

$$(ii)\ \log_{10}P=-\frac{L_0}{RT}+1.75\ \log_{10}T-\frac{b}{R}T+i'$$

13.7. The Entropy and the Chemical Constant

It is also possible to obtain a relation between the vapour pressure constant and the entropy of a substance.

Suppose we start with a gm-mole of a pure solid substance at absolute zero and finally convert it into vapour at a temperature T under a standard pressure P_0 (usually one atmosphere). Let us calculate the entropy-change of the transformation.

Firstly, the solid is heated from 0° to T°K, $\triangle S_1 = \int_0^T C_{P_c}\, d\ln T$

Secondly, the solid is vaporised at T°K, $\triangle S_2 = \frac{L_T}{T}$

Finally, the vapour is changed from its own vapour pressure P to the standard pressure P_0, $\triangle S_3 = R\ln\frac{P}{P_0}$

Hence, net entropy-change,

$$S_{T\,(\text{gas})} - S_{0\,(\text{cond})} = \triangle S = \triangle S_1 + \triangle S_2 + \triangle S_3$$

i.e.,

$$\triangle S = \int_0^T C_{P_c}\, d\ln T + \frac{L_T}{T} + R\ln\frac{P}{P_0}$$

or

$$R\ln\frac{P}{P_0} = -\frac{L_T}{T} - \int_0^T C_{P_c}\, d\ln T + \triangle S$$

$$= -\frac{L_0 + \int_0^T C_{P_g}\, dT - \int_0^T C_{P_c}\, dT}{T} - \int_0^T C_{P_c}\, d\ln T + \triangle S$$

Since, $P_0 = 1$, $\ln P = -\frac{L_0}{RT} - \frac{1}{RT}\int_0^T C_{P_g}\, dT + \frac{1}{RT}\int_0^T C_{P_c}\, dT$

$$-\frac{1}{R}\int_0^T C_{P_c}\, d\ln T + \frac{S_T - S_0}{R}$$

$$= -\frac{L_0}{RT} - \frac{5}{2} + \frac{1}{RT}\int_0^T C_{P_c}\, dT - \frac{1}{R}\int_0^T C_{P_c}\, d\ln T + \frac{S_T - S_0}{R}$$

$[\because C_{P_g} = \frac{5}{2}R$

Hence, $\log_{10} P = -\frac{L_0}{2.303RT} - \frac{5}{2\times 2.303} + \frac{1}{2.303RT}\times$

$$\int_0^T C_{P_c}\, dT - \frac{1}{2.303\,R}\int_0^T C_{P_c}\, d\ln T + \frac{S_T - S_0}{R\times 2.303} \quad \ldots (13.19)$$

Comparing equations (13.18) and (13.19),

$$\frac{-5}{2\times 2.303}+\frac{S_T-S_0}{R\times 2.303}=\tfrac{5}{2}\log_{10}T+i$$

or $$S_T=S_0+\tfrac{5}{2}R+\tfrac{5}{2}R\times 2.303\log_{10}T+2.303\,R\times i$$

From the third law of thermodynamics, $S_0=0$, *i.e.*, entropy of a pure solid at 0°K is zero.

$$\therefore\quad S_T=\tfrac{5}{2}R+\tfrac{5}{2}R\times 2.303\ \log_{10}T+2.303\ R\times i \qquad \ldots (13.20)$$

The knowledge of chemical constant thus predicts the value of entropy of a pure monatomic vapour.

The statistical expression for entropy (Sec. 11.9) for a monatomic gas at temp. T and pressure = 1 atm,

$$S_T=\tfrac{5}{2}R+\tfrac{5}{2}R\ln T+R\ln\frac{(2\pi MkT)^{3/2}k}{N^{3/2}h^3}$$

We may compare with equation (13.20), when

$$i=\log_{10}\frac{(2\pi MkT)^{3/2}k}{N^{3/2}h^3}$$

The values of i determined from vapour-pressure formula and calculated as above show remarkable identity.

TABLE : VAPOUR PRESSURE CONSTANTS (P in atm.)

Gas	i (calc)	i (obs.)	Gas	i (calc)	i (obs)	Gas	i (calc)	i (obs)
He	−0.68	−0.69	Zn	1.136	1.26	N_2	−0.175	−0.19
Ar	0.81	0.83	Cu	1.11	1.40	O_2	0.53	0.57
Na	0.757	0.78	Hg	1.87	1.99	Cl_2	1.35	1.74
K	1.02	1.13	Cd	1.49	1.57	I_2	2.99	3.10
Mg	0.49	0.49	Tl	2.18	2.40	HCl	−0.42	−0.43

The observed and calculated values of entropy are also the same.

TABLE : ENTROPY VALUES OF MONATOMIC VAPOURS

Gas→	Zn	Mg	Cn
S (Calc.)	38.4	35.5	39.7
S (Obs.)	38.5	35.3	37.8

13.8. Second Order Transitions : Ehrenfest Equations

The phase-changes commonly met with such as sublimation, melting, vaporisation etc. are termed '*first order transitions*'. These changes of phase are always associated with an abrupt change in volume and in entropy at the point of transformation. At equilibrium, however, when transition occurs, the Gibbs potential G remains unaltered. We have therefore the following criteria for the first order transitions ; the suffixes i and f denote the initial phase and the final transformed phase.

(*a*) $G_i = G_f$ (*b*) $V_f - V_i \neq 0$

Since $dG = VdP - SdT$,

then $$\left(\frac{\partial G_f}{\partial P}\right)_T - \left(\frac{\partial G_i}{\partial P}\right)_T = V_f - V_i \neq 0$$

(*c*) $S_f - S_i \neq 0$

$$\therefore \quad \left(\frac{\partial G_i}{\partial T}\right)_P - \left(\frac{\partial G_f}{\partial T}\right)_P = S_f - S_i \neq 0 \qquad \ldots (13.21)$$

Graphically these may be represented as in Fig. 13*d*.

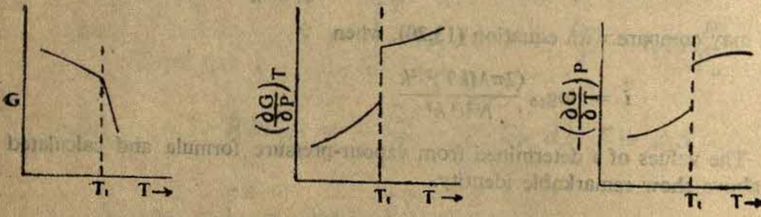

Fig. 13*d*. First-order transitions.

That is, at the transition point *first order derivatives* of the Gibbs potential change discontinuously.

On the other hand, a few cases are known in which when the substance changes from one phase to another, no latent heat is absorbed or evolved, *i.e.*, there is no change in entropy. Besides, during the change there is no abrupt or discontinuous change in volume. Such changes of phase are called the '*Second order transitions*'. Illustrations may be found in the transformation of

(*a*) liquid Helium II to liquid Helium I, at the λ-point,

(*b*) ferro-magnetic material to paramagnetic material at the Curie point,

(*c*) super-conductor to an ordinary conductor.

The criteria for the second-order transitions are

(*i*) $G_f = G_i$

(*ii*) $$\left(\frac{\partial G_f}{\partial P}\right)_T - \left(\frac{\partial G_i}{\partial P}\right)_T = V_f - V_i = 0 \qquad \ldots (13.22)$$

$$(iii) \qquad \left(\frac{\partial G_i}{\partial T}\right)_P - \left(\frac{\partial G_f}{\partial T}\right)_P = S_f - S_i = 0$$

Graphically represented, these would take the form as in Fig. 13*e*. The first order derivatives are the same at the transition point.

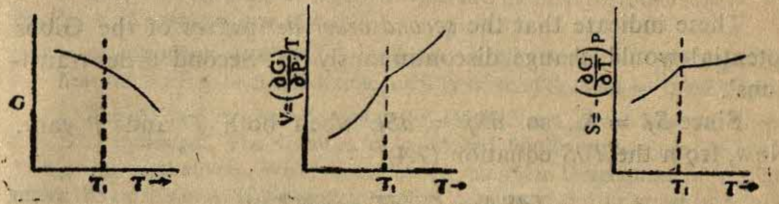

Fig. 13*e*. Second order transitions

The change of phase is manifest, *in the absence of any latent heat change*, by the abrupt variation in various properties of the substance, like specific heat, coefficient of expansion, etc. The curves in the figure 13*f* represent specific heat and density changes of liquid Helium from state I to II at the λ-point. The discontinuity of these properties at the transition point is obvious.

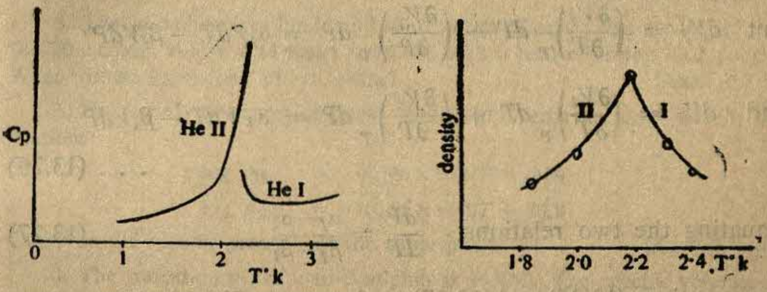

Fig. 13*f*. Transition of liquid Helium

In these cases, C_p-values change discontinuously, so,

$$C_{p_f}-C_{p_i}=T\left(\frac{\partial S_f}{\partial T}\right)_P-T\left(\frac{\partial S_i}{\partial T}\right)_P=T\left(\frac{\partial^2 G_i}{\partial T^2}\right)_P-T\left(\frac{\partial^2 G_f}{\partial T^2}\right)_P$$

$$\text{or} \quad \left(\frac{\partial^2 G_i}{\partial T^2}\right)_P-\left(\frac{\partial^2 G_f}{\partial T^2}\right)_P=\frac{C_{p_f}-C_{p_i}}{T} \qquad \ldots (13.23)$$

Similarly, for coefficient of expansion,

$$\alpha_f - \alpha_i = \frac{1}{V}\left(\frac{\partial V_f}{\partial T}\right)_P - \frac{1}{V}\left(\frac{\partial V_i}{\partial T}\right)_P$$

or $$V(\alpha_f - \alpha_i) = \left[\frac{\partial^2 G_f}{\partial T \partial P}\right] - \left[\frac{\partial^2 G_i}{\partial T \partial P}\right] \qquad \ldots (13.24)$$

These indicate that the *second order derivatives* of the Gibbs potential would change discontinuously in 'Second order transitions'.

Since $S_f = S_i$, so $dS_f = dS_i$, when both T and P vary. Now, from the TdS equation (7.4),

$$TdS_f = C_{p_f}dT - \alpha_f VTdP$$

and $$TdS_i = C_{p_i}dT - \alpha_i VTdP$$

Equating these, $$\frac{dP}{dT} = \frac{C_{p_f} - C_{p_i}}{TV(\alpha_f - \alpha_i)} \qquad \ldots (13.25)$$

Again, since $V_f = V_i$, so $dV_f = dV_i$, when both T and P vary.

But $$dV_f = \left(\frac{\partial V_f}{\partial T}\right)_P dT + \left(\frac{\partial V_f}{\partial P}\right)_T dP = \alpha_f VdT - \beta_f VdP$$

and $$dV_i = \left(\frac{\partial V_i}{\partial T}\right)_P dT + \left(\frac{\partial V_i}{\partial P}\right)_T dP = \alpha_i VdT - \beta_i VdP \qquad \ldots (13.26)$$

Equating the two relations, $$\frac{dP}{dT} = \frac{\alpha_f - \alpha_i}{\beta_f - \beta_i} \qquad \ldots (13.27)$$

The equations (13.25) and (13.27) are known as *Ehrenfest's equations*, and are analogous to the Clausius-Clapeyron equations.

Problems

1. What is the approx. boiling pt. of water at a place where the atmospheric pressure is 600 mm? (l = 539 cal/gm) [Ans: 93.4°C]

2. (*a*) What will be the vapour pressure of water at 95°C, if L = 9720 cal/mole

(*b*) What pressure would be required to lower the freezing pt. of ice by 2.0°C? [Ans: (*a*) 636 mm (*b*) 267 atm]

3. T_b is the normal boiling pt. of a liquid and $\triangle T$ is the increase in boiling pt when the pressure is raised by $\triangle P$ (atm). Show that

$$\frac{\triangle T}{T_b} = \frac{\triangle P}{10.5}$$

4. Show that the pressure required to increase the m. pt. of sodium ($M = 23$) by 1°C is 135 atmospheres. Given

m. pt. of sodium = 97.6°C, density of liq. Sodium = 0.929 gm/c.c.
heat of fusion = 3.05 kJ/mole, density of solid Sodium = 0.952 gm/c.c.

5. The normal m. pt. of sulphur = 119.0°C and latent heat of fusion l = 55.2 joules/gm. The densities of solid and liquid sulphur are 2.05 and 1.81 gm/cc. respectively. What should be the minimum temperature of sulphur under the earth's crust if the molten sulphur is pumped out by steam at a total pressure of 6 atmospheres. [Ans. 119.23°C]

6. Calculate the change in the melting pt. of ice brought about by application of 100 atm. pressure. The volume change in melting is -1.63×10^{-3} litre/mole and the enthalpy of fusion is 1440 cal/mole. [Ans. − 0.75°C]

7. When one Kg of diphenyl melts (m.pt. 54°C) the increase in volume is 95.8 c.c. Its melting point increases by 2.7×10^{-2} °C for every one atmosphere increase in pressure. Calculate the latent heat of fusion of diphenyl.

[Ans. 4745 cal/mole]

8. The sp. volumes of liquid and solid forms of acetic acid are 0.9315 and 0.7720 c.c./gm. Acetic acid melts at 16.6°C with a heat of fusion 43.2 cal/gm. What will be its melting pt. at 5 atm? [Ans. 16.7°C]

9. The vapour pressures of liquid and solid arsenic are expressed by the relations:

$$\log p_{\text{liq}} = -(2.46\times10^3)/T + 6.69$$

$$\log p_{\text{solid}} = -(6.95\times10^3)/T + 10.8$$

Compute the vapour pressure at the triple point. [Ans. 36 atm.]

10. The transition pt. of α to β-sulphur is 96.6°C. The specific volumes of α and β sulphur are 0.495 and 0.505 c.c. respectively. The heat of transition = 75 cal/gm-atom. What will be the transition temp. at 25 atm. pressure?

11. If p_1 and p_2 be the vapour pressure of a liquid under total pressures P_1 and P_2, at a given temperature T. Show that

$$RT\ln\frac{p_2}{p_1} = v\,(P_2-P_1)$$

where v = molar volume of the liquid.

The vap-pressure of water is 23.756 mm at 25°C. What will be the vap-pressure at the same temperature, when the total pressure exerted over water is ten atmospheres? [Ans. p_2 = 23.93 mm.]

12. What is the latent heat of fusion of tin (m.pt. 504°K), if its m.pt. is raised by 0.328°C when pressure is increased by 10 atm? The volume-change is 0.03894 c.c./gm. [Ans. 14.48 cal/gm.]

13. At one atm. mercury melts at −38.87°C and its density is 13.69 gm/c.c. The density of the solid is 14.19 gm/c.c. The heat of fusion is 2.33 cal/gm. What would be the m.pt of mercury at 1000 atm.? [Ans. −32.6°C]

14. The density of solid and liquid phenol (m.pt. 41°C) are 1.072 and 1.056 gm/c.c. Estimate the change in m.pt. if the pressure is raised to 10 atm. ($l_f = 25$ cal/gm).

15. The heat of vaporisation of cyclohexane (b. pt. 80°C) is 85 cal/gm. The specific densities of liquid and vapour are 0.72 and 0.003 gm at this temperature. Find out the pressure at which the liquid can be distilled at 60°C.

CHAPTER 14

THE CHEMICAL EQUILIBRIUM

14.1. Equilibrium : The Law of Mass Action

It is common knowledge that many reactions do not go to completion even if favourable external conditions are maintained. The reactions proceed to some extent and then they come to a stop. A portion of the reactants, sometimes a considerable portion, remain unaltered in the system. For example, in the reaction,

$$H_2 + I_2 \rightleftharpoons 2HI,$$

if some hydrogen and iodine vapour be kept at a constant temperature in a closed vessel, only a portion of these will be converted into hydrogen iodide, and then the reaction would stop. A mixture of hydrogen iodide, iodine and hydrogen will remain in the vessel for unlimited time, temperature being kept constant. On the other hand, if at the same temperature, some hydrogen iodide be taken in a closed vessel, a fraction will decompose into hydrogen and iodine and the rest of hydrogen iodide will remain intact. The proportions of hydrogen, iodine and hydrogen iodide in the mixture will be the same finally in both the experiments. When such a stage is reached in the course of a reaction that no further action is apparent, it is said to have attained *equilibrium* at that temperature. It is obvious that the reaction can proceed either way and the composition of the system at eqm. is fixed. The cessation of chemical reaction is however only apparent. In fact, when equilibrium is attained, the reactions proceed in both directions at equal rates, so that the amount of reactants disappearing per unit time is reproduced from the action in opposite direction. The equilibrium is thus really a dynamic one, not static. The reactions proceeding in both directions are called '*reversible reactions*'. The reversibility is indicated with double arrows in opposite direction.

A quantitative relation between the amounts of the reactants and the resultants at eqm. was developed from a basic principle, called the Law of Mass Action, first enunciated by two Norwegian chemists, Guldberg and Waage (1867).

The law states : *At a constant temperature, the rate of a chemical* *reaction is proportional to the 'active masses' of the reacting substances.* The expression 'active mass' in the statement requires serious consideration. For ordinary systems as those of gases or dilute solutions, which do not deviate appreciably from ideal behaviour, active mass may be taken to mean *molar concentration.* For solids and pure liquids, the active masses or concentrations are taken as unity since the rate of reaction is independent of their amounts present.

Consider a reversible reaction ; $\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}$

$$\textit{Conc:} \quad C'_A \quad C'_B \quad C'_C \quad C'_D$$

Let C'-terms denote the concentrations of the components at a given instant during the progress of the reaction. According to the law, the rate of reaction (R_{AB}) between A and B at that moment will be

$$R_{AB} = k_1 C'_A \,.\, C'_B$$

where k_1, the constant of proportionality, depends upon reactants and temperature. The concentrations of the reactants (A and B) would diminish with the progress of reaction and hence its rate would diminish with time.

Similarly, the rate of the opposite reaction (R_{CD}) between C and D at that moment will be

$$R_{CD} = k_2 C'_C \cdot C'_D$$

With the progress of reaction, the concentrations of C and D would increase and hence the rate R_{CD} would increase with time. A time will come when the rates of reaction in the two opposite directions would be equal, *i.e.*, $R_{AB} = R_{CD}$. The system would then attain equilibrium and there would be no further change in the masses of the components of the system. At equilibrium, let the concentrations be expressed by C-terms (instead of C'). Then,

$$R_{AB} = R_{CD}$$

or

$$k_1 C_A C_B = k_2 C_C C_D$$

or

$$\frac{C_C C_D}{C_A C_B} = \frac{k_1}{k_2} = K_C \text{ (constant)} \qquad \ldots (14.1)$$

K_C is called the *equilibrium constant of the reaction.*

The initial concentrations may be varied but at a given temperature, equation (14.1) will be valid for any given reversible reaction. Furthermore, the state of equilibrium can be reached starting either with A and B or with C and D.

In the case cited above one molecule only of each of the reactants was involved. In general, let us take an example now with more than one molecule of a species entering into the reaction, of reversible type, represented as,

$$aA + bB + cC + \ldots \rightleftharpoons dD + eE + fF + \ldots$$

Then the equilibrium constant, $K_C = \dfrac{C_D^d\, C_E^e\, C_F^f \ldots .}{C_A^a\, C_B^b\, C_C^c \ldots .}$ . . . (14.2)

That is, the coefficients in the stoichiometric equation become powers of respective concentrations in the expression for equilibrium constant.

14.2 Equilibrium constant from thermodynamic considerations

The expression for the equilibrium constant can easily be arrived at from thermodynamic considerations.

Suppose, the reaction,

$$aA + bB + cC + \ldots = dD + eE + fF + \ldots$$

has attained equilibrium at a temperature T. Let G denote the thermodynamic potential or free energy of the system.

Now, consider a small chemical change in the system under conditions of equilibrium such that the reactants A, B, etc. diminish by minute amounts such as $a\triangle x$, $b\triangle x$, . . . $c\triangle x$ . . . gm-moles. In consequence, the resultants D, E, etc. will increase by the amounts $d\triangle x$, $e\triangle x$, $f\triangle x$, etc.

By Gibbs and Duhem relation, we can express the change in thermodynamic potential of the system, $\triangle G$, by the chemical potentials μ of the components. Thus,

$$dG = \Sigma\mu dn = \mu_D.d\triangle x + \mu_E.e\triangle x + \mu_F.f\triangle x \ldots - \mu_A.a\triangle x \\ - \mu_B.b\triangle x - \ldots$$

At equilibrium, $dG = 0$, hence

$$\mu_D.d\triangle x + \mu_E.e\triangle x + \mu_F.f\triangle x + \ldots = \mu_A.a\triangle x + \mu_B.b\triangle x \\ + \mu_C.c\triangle x + \ldots$$

or $$d\mu_D + e\mu_E + f\mu_F + \ldots = a\mu_A + b\mu_B + c\mu_C + \ldots$$

Expressing chemical potentials in terms of activities (a) ;

$$(\mu = RT\, ln\, a + z^{*}), \text{ we have}$$

$$d[RT\, ln\, a_D + z_D] + e[RT\, ln\, a_E + z_E] + f[RT\, ln\, a_F + z_F] + \ldots$$
$$= a[RT\, ln\, a_A + z_A] + b[RT\, ln\, a_B + z_B] + c[RT\, ln\, a_C + z_C] + \ldots$$

$$\text{or, } RT\, ln\, a_D^d + RT\, ln\, a_E^e + RT\, ln\, a_F^f \ldots - RT\, ln\, a_A^a - RT\, ln\, a_B^b - RT\, ln\, a_C^c - \ldots$$
$$= az_A + bz_B + cz_C + \ldots - dz_D - ez_E - fz_F \ldots = z' \text{ (constant)}$$

$$\text{or } ln\, \frac{a_D^d \times a_E^e \times a_F^f \times \ldots}{a_A^a \times a_B^b \times a_C^c \times \ldots} = \frac{z'}{RT} = z \text{ (constant, since } T \text{ is constant)}$$

$$\text{Therefore,} \quad \frac{a_D^d \times a_E^e \times a_F^f \times \ldots}{a_A^a \times a_B^b \times a_C^c \times \ldots} = k_a \qquad \ldots (14.3)$$

where K_a is the thermodynamic equilibrium constant. It is expressed in terms of the activities of the components and therefore it is valid for all systems, ideal or not.

The activities are related to concentrations as

$$a = \gamma x \qquad \text{and} \qquad a = fc$$

where γ and f are the activity coefficients and x and c denote concentrations in mol-fraction and molarity basis respectively at eqm. Substituting these in eqn. (14.3),

$$(i)\ \frac{x_D^d \times x_E^e \times x_F^f \times \ldots}{x_A^a \times x_B^b \times x_C^c \times \ldots} \times \frac{\gamma_D^d \times \gamma_E^e \times \gamma_F^f \times \ldots}{\gamma_A^a \times \gamma_B^b \times \gamma_C^c \times \ldots} = K_a \qquad \ldots (14.4)$$

$$(ii)\ \frac{C_D^d \times C_E^e \times C_F^f \times \ldots}{C_A^a \times C_B^b \times C_C^c \times \ldots} \times \frac{f_D^d \times f_E^e \times f_F^f \times \ldots}{f_A^a \times f_B^b \times f_C^c \times \ldots} = K_a \qquad \ldots (14.5)$$

In ideal systems, the activity coefficients are equal to unity. For practical purposes in approximate valuations, dilute solutions or gas-mixtures are supposed to behave almost ideally. In such circumstances, equation (14.5) may be written as,

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* Constant $z = \mu^{\circ}$, the chemical potential under standard states.

$$\frac{C_D^d \times C_E^e \times C_F^f \times \ldots}{C_A^a \times C_B^b \times C_C^c \times \ldots} = K_a = K_C \text{(say)} \qquad \ldots (14.6)$$

It is the same relation as empirically derived in eqn. 14.2. It is thus a consequence of the laws of thermodynamics.

Gaseous reactions. In a gaseous reaction, components are usually expressed in terms of their partial pressures instead of molarities. If the gases are supposed to behave ideally, we have the activities equal to the fugacities. Further, the fugacities may be replaced by the partial pressures of the components, such as P_A, P_B, ... P_D, P_E ... etc.

Then the total pressure, $P = P_A + P_B + \ldots + P_D + P_E + \ldots$

The equilibrium constant, $K_a = \dfrac{a_D^d \times a_E^e \times \ldots}{a_A^a \times a_B^b \times \ldots}$

Then, in terms of fugacities, $K_f = \dfrac{\mathbf{f}_D^d \times \mathbf{f}_E^e \times \ldots}{\mathbf{f}_A^a \times \mathbf{f}_B^b \times \ldots}$

Replacing **f** by P, in ideal systems, the equilibrium constant, K_P, is given by

$$K_P = \frac{P_D^d \times P_E^e \times \ldots}{P_A^a \times P_B^b \times \ldots} \qquad \ldots (14.7)$$

Again, assuming ideality, we can express pressures as

$$P_A = C_A RT, \qquad P_B = C_B RT, \text{ etc.}$$

Hence $$K_P = \frac{(C_D RT)^d \times (C_E RT)^e \times \ldots}{(C_A RT)^a \times (C_B RT)^b \times \ldots}$$

$$= \frac{C_D^d \times C_E^e \times \ldots}{C_A^a \times C_B^b \times \ldots} \times (RT)^{d+e+\ldots-a-b\ldots}$$

or, $$K_P = K_C (RT)^{\Delta\nu}, \qquad \ldots (14.8)$$

in which $\Delta\nu$ = no. of resultant molecules — no. of reactant molecules. It is a relation between the equilibrium constants derived from partial pressure units and from molar concentration units of components.

The partial pressures can be expressed in terms of the total pressure (P) and the respective mole-fractions ; such as, $P_A = x_A P$, $P_B = x_B P$, etc. Then, eqn. (14.7) can be changed as,

$$K_P = \frac{(x_D P)^d \times (x_E P)^e \times \ldots}{(x_A P)^a \times (x_B P)^b \times \ldots}$$

$$= \left\{ \frac{x_D^d \times x_E^e \times \ldots}{(x_A)^a \times (x_B)^b \times \ldots} \right\} \times P^{(d+e+\ldots-a-b\ldots)}$$

Writing K_x for the terms within the parenthesis,

$$K_p = K_x P^{\Delta\nu} \quad \text{or} \quad K_x = K_p / P^{\Delta\nu} \qquad \ldots (14.9)$$

It should be mentioned here that the value of K_p (or K_c) is independent of pressure and does not change with total pressure or partial pressure variations. But the magnitude of K_x would vary with pressure except when $\Delta\nu = 0$.

14.3. Equilibrium Constants of Some Typical Reactions

(*a*) *Water gas reaction* : $H_2 + CO_2 \rightleftharpoons H_2O + CO$

Starting with equimolecular mixture of the reactants, we have, when x is the extent of H_2 used up at eqm.,

	H_2	CO_2	H_2O	CO	=	Total
Moles at eqm. :	$1-x$	$1-x$	x	x	=	2
Partial Pressures :	$\frac{1-x}{2}P$	$\frac{1-x}{2}P$	$\frac{x}{2}P$	$\frac{x}{2}P$	=	P

$$K_P = \frac{p_{H_2O} \times p_{CO}}{p_{H_2} \times p_{CO_2}} = \frac{\left(\frac{x}{2}P\right)^2}{\left(\frac{1-x}{2}P\right)^2} = \frac{x^2}{(1-x)^2}$$

hence x is independent of pressure.

At 1260°K and 1 atmosphere, the eqm. composition of this reaction is $CO_2 = 21.4$, $H_2 = 22.9$ and $CO = 27.8$ (moles per cent).

$$\text{Hence} \quad K_P = \frac{p_{H_2O} \times p_{CO}}{p_{CO_2} \times p_{H_2}} = \frac{(27.8)^2}{(21.4) \times (22.9)} = 1.58$$

(*b*) *The dissociation of nitrogen tetroxide*, $N_2O_4 \rightleftharpoons 2NO_2$

So, we have, $K_P = p^2_{NO_2} / p_{N_2O_4}$

If we start with 1 mole of N_2O_4 and α be the degree of dissociation, then at eqm., there are in all $(1 + \alpha)$ gm-moles of gas, of which 2α gm-moles are NO_2 and $(1-\alpha)$ gm-moles N_2O_4.

Hence $$K_x = \frac{[2\alpha/(1+\alpha)]^2}{[(1-\alpha)/(1+\alpha)]} = \frac{4\alpha^2}{1-\alpha^2}$$

But $$K_P = K_x.P^{\Delta\nu}, \quad \text{(from eqn 14.9)}$$

Since, $$\Delta\nu = 1, \quad K_P = \frac{4\alpha^2}{1-\alpha^2}P$$

'α' can be easily obtained from vapour-density measurements and hence K_P is evaluated.

(*c*) *Synthesis of ammonia* : $N_2 + 3H_2 \rightleftharpoons 2NH_3$

This is a reaction in which the number of molecules of resultants is less than that of the reactants. Suppose we start with a mixture of N_2 and H_2 in 1 : 3 ratio in moles and let the extent of chemical transformation at equilibrium be x per mole of nitrogen. Then

	N_2	H_2	NH_3	Total
Initial moles	1	3	0	= 4
Moles at equilibrium	$1-x$	$3-3x$	$2x$	$= 4-2x$
Partial pressures	$\frac{1-x}{4-2x}P$	$\frac{3-3x}{4-2x}P$	$\frac{2x}{4-2x}P$	$= P$

So, $$K_P = \frac{P^2_{NH_3}}{P_{N_2}\,.\,P^3_{H_2}} = \frac{\left[\frac{2x}{4-2x}P\right]^2}{\left[\frac{1-x}{4-2x}P\right]\left[\frac{3-3x}{4-2x}P\right]^3} = \frac{4x^2(4-2x)^2}{27(1-x)^4P^2}$$

If x is small, $$K_P \approx \frac{64}{27}\cdot\frac{x^2}{P^2}$$

It shows K_P, which is constant at any given temperature, is determined by the ratio x/P. Further, with increase of P, x must also increase proportionately,

for $$P^2 = \frac{64}{27K_P}\cdot x^2, \ \textit{i.e.,} \ P = k'x$$

This means that with higher pressures, the yield of ammonia would be larger. This is a valuable information to the manufacturer of ammonia. We can also calculate K_C from this, by equation (14.8),

$$K_C = K_P(RT)^{-\Delta\nu} = \frac{64x^2}{27}\frac{1}{P^2}(RT)^{-(2-4)} = \frac{64x^2}{27}(RT/P)^2$$

Since volume $V = (4-2x)\frac{RT}{P} \approx 4\frac{RT}{P}$, we have,

$$K_C = \frac{64x^2}{27}\left(\frac{V}{4}\right)^2 = \frac{4x^2V^2}{27}$$

(*d*) *Hydrogen from reduction of steam.*

(*i*) with iron : $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$

when $K_a = \frac{a_{Fe_3O_4}\times a^4_{H_2}}{a^3_{Fe}\times a^4_{H_2O}} = \left(\frac{a_{H_2}}{a_{H_2O}}\right)^4 \approx \left[\frac{P_{H_2}}{P_{H_2O}}\right]^4$

Thus the ratio of P_{H_2}/P_{H_2O} is constant, which has been substantiated from experiment. This means that with increase of steam-pressure higher yield of hydrogen is obtained.

(*ii*) with carbon : $C + H_2O \rightleftharpoons CO + H_2$

where $K_a = \frac{a_{CO}\times a_{H_2}}{a_C\times a_{H_2O}} \approx \frac{P_{CO}\times P_{H_2}}{P_{H_2O}} = \frac{P^2_{H_2}}{P_{H_2O}}$, (since $P_{CO} = P_{H_2}$)

Hence, $K_P = \frac{P^2_{H_2}}{P_{H_2O}}$, *i.e.*, $P_{H_2} \infty \sqrt{P_{H_2O}}$

14.4. Influence of Inert Gases on the Equilibrium of Gaseous Reactions

It would be of interest to know if the eqm. concentrations of the components would alter by the presence of some inert gases *i.e.*, gases which do not interact chemically with the components.

Consider a gaseous reaction : $aA + bB \rightleftharpoons cC + dD$

Let x_A, x_B, x_C, x_D denote the mole-fractions of the components at eqm. At a constant temperature, the eqm. constant K_P remains constant (see eqn. 14.9).

Now $K_p = K_x\,(P)^{\Delta\nu}$

$$= \left(\frac{x^c_C\times x^d_D}{x^a_A\times x^b_B}\right)(P)^{\Delta\nu}$$

Let n_0 gm-moles of an inert gas be introduced into the system. If n-terms denote the gm-moles of the components, then

$$x_A = \frac{n_A}{n_0 + n_A + n_B + n_C + n_D} = \frac{n_A}{\Sigma n}, \quad \Sigma n = \text{total number}$$

of moles.

Similarly, $x_B = \dfrac{n_B}{\Sigma n}$; $x_C = \dfrac{n_C}{\Sigma n}$, etc.

Hence
$$K_p = \frac{(n_C/\Sigma n)^c \times (n_D/\Sigma n)^d}{(n_A/\Sigma n)^a \times (n_B/\Sigma n)^b} \times (P)^{\Delta\nu}$$

$$= \left[\frac{n_C^c \times n_D^d}{n_A^a \times n_B^b}\right] \times \left(\frac{P}{\Sigma n}\right)^{\Delta\nu} \quad \ldots (A)$$

The introduction of an inert gas would always increase Σn. The effect may be considered separately in different cases.

I. When the inert gas is added at *constant pressure* :

(*a*) For a reaction in which $\Delta\nu = 0$, $(P/\Sigma n)^{\Delta\nu} = 1$. Hence in such a reaction the first term $\left[\dfrac{n_C^c \times n_D^d}{n_A^a \times n_B^b}\right]$ of eqn (A) will remain unaltered to keep K_p constant. That is, the eqm. remains undisturbed.

(*b*) For a reaction in whcih $\Delta\nu$ is positive, $(P/\Sigma n)^{\Delta\nu}$ diminishes with increase in Σn ; hence the first factor of eqn. (A) will increase in magnitude to keep K_p constant. This is possible by increasing the concentrations of resultants in the numerator and decreasing the concentrations in the denominator. In other words, there would be more of the reaction. At constant pressure, the presence of nitrogen would increase the dissociation of phosphorus pentachloride.

(*c*) For a reaction in which $\Delta\nu$ is negative, $(P/\Sigma n)^{\Delta\nu}$ increases with increase in Σn ; hence the first factor must diminish to keep K_p constant. In other words, the concentrations of the resultants in the numerator must decrease. That is, the reaction will be depressed. So, at constant pressure the presence of argon would reduce the formation of ammonia from nitrogen and hydrogen.

II. When the inert gas is added at *constant volume* :

If the inert gas is added at constant volume, the total pressure P will increase proportionately with Σn; hence $(P/\Sigma n)$ will remain constant. Therefore, the first factor in equation will remain unchanged to keep K_p constant. That is, the equilibrium will not be disturbed, if a foreign gas is added at constant volume.

14-5. Some Typical Numerical Examples

Problem 1. At room temperature and 1 atm total pressure one N_2O_4 molecule in six is dissociated. Calculate K_p.

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$1-\alpha \qquad 2\alpha\ , \qquad (\alpha, \text{ degree of dissociation})$$

$$\text{Partial pressure at eqm} \quad \frac{1-\alpha}{1+\alpha}P \quad \frac{2\alpha}{1+\alpha}P$$

$$K_p = P^2_{NO_2}/P_{N_2O_4} = \frac{4\alpha^2P^2/(1+\alpha)^2}{P(1-\alpha)/(1+\alpha)} = \frac{4\alpha^2P}{1-\alpha^2} \qquad \ldots \text{(A)}$$

Here $\alpha = \frac{1}{6} = 0.167$

$$\therefore \quad K_p = \frac{4\times(0.167)^2\times1}{1-(0.167)^2} = 0.114$$

From eqn (A), $\alpha = \left(\dfrac{K_p}{K_p+4P}\right)^{\frac{1}{2}}$, hence

if P is very large, α will be negligible i.e. hardly any dissociation would occur. If P is very low, α tends to unity, so that almost complete dissociation would occur.

Problem 2. In the gaseous reaction, $X + 2Y \rightarrow XY_2$, $K_p = 2.5 \times 10^{-4}$ atm^{-2} at 100°C. Two moles of Y and 1 mole of X are mixed. What total pressure would be required to convert 50% of X into XY_2.

At eqm, moles of $X = (1-0.5) = 0.5$, moles of $Y = (2-1) = 1.0$

and moles of $XY_2 = 0.5$. So, total moles at eqm $= 2.0$

Let total pressure be P.

$\therefore$ Partial pressures are, $P_x = 0.25P$, $P_y = 0.5P$, $P_{xy_2} = 0.25P$

$$\therefore K_p = \frac{P_{xy_2}}{P_x \times P_y{}^2} = \frac{0.25P}{0.25P\times(0.5P)^2} = \frac{1}{0.25P^2}$$

$$\therefore \quad P = \left(\frac{1}{0.25\times K_p}\right)^{\frac{1}{2}} = \left(\frac{1}{0.25\times2.5\times10^{-4}}\right)^{\frac{1}{2}} = 126.4 \text{ atm.}$$

Problem 3. At 25°C, 1 mole of acetic acid and 1 mole of ethanol are mixed. At eqm. 0.667 moles of acid have reacted. Calculate K_C. How much ester would be obtained if 2 moles of acid were taken with 1 mole ethanol under the same conditions?

$$K_C = \frac{C_{\text{ester}} \times C_{H_2O}}{C_{\text{acid}} \times C_{\text{alcohol}}} = \frac{(0.667/V)\,(0.667/V)}{(0.333/V)\,(0.333/V)} = 4.00$$

In the other experiment, let x moles of acid be transformed, then

$$\begin{array}{lcccc} & CH_3COOH \; + & EtOH & \rightleftharpoons \; CH_3COOEt & + \; H_2O \\ \text{Conc :} & (2-x)/V & (1-x)/V & x/V & x/V \end{array}$$

$$\therefore \qquad K_C = 4 = \frac{x^2}{(2-x)\,(1-x)} = \frac{x^2}{2-3x+x^2}$$

whence $x = 3.15$ or 0.85.

Since the first solution is absurd, amount of ester at eqm. is 0.85 moles.

Problem 4. At 1000°K for the equilibria,

(*i*) $CaCO_3 \rightleftharpoons CaO+CO_2$, $K_P = 4.0 \times 10^{-2}$ atm.
(*ii*) $C+CO_2 \rightleftharpoons 2CO$, $K_P' = 2.0$ atm.

Solid carbon, CaO and $CaCO_3$ are mixed and allowed to attain eqm. at 1000°K. What is the pressure of CO?

$$K_P = \frac{a_{CaO} \times a_{CO_2}}{a_{C_aCO_2}} \approx P_{CO_2}\,;\; K'_P = \frac{a^2_{CO}}{a_C \cdot a_{CO_2}} = \frac{P^2_{CO}}{P_{CO_2}}$$

$$\therefore \quad K_P \cdot K'_P = P^2{}_{CO} \;\text{ or }\; P_{CO} = \sqrt{K_P \cdot K'_P} = \sqrt{4 \times 10^{-2} \times 2.0}$$
$$= 0.28 \text{ atmospheres.}$$

Problem 5. At 1000°C, the pressure of iodine gas is found to be 0.112 atm. whereas the expected pressure is 0.074 atm. The increased pressure is due to dissociation ; $I_2 \rightleftharpoons 2I$. Calculate K_P. Also find out the pressure at which I_2 will be 90% dissociated at 1000°C.

$$\begin{array}{ccc} I_2 \rightleftharpoons & 2I & \text{Total} \\ 1-\alpha & 2\alpha & 1+\alpha\,; \end{array} \qquad \alpha = \text{degree of dissociation.}$$

Since pressure is proportional to number of moles of entities of gases ; $P/P_0 = 1 + \alpha$, where P = observed pressure, P_0 = calculated pressure (having no dissociation).

$$\therefore \quad \alpha = \frac{P-P_0}{P_0}$$

Now $\quad P_I = \dfrac{2\alpha}{1+\alpha} P\,; \quad P_{I_2} = \dfrac{1-\alpha}{1+\alpha} P$

Hence $$K_P = \frac{\left[\frac{2\alpha}{1+\alpha}P\right]^2}{\left(\frac{1-\alpha}{1+\alpha}P\right)} = \frac{4\alpha^2}{1-\alpha^2}P = \frac{4\left(\frac{P-P_0}{P_0}\right)^2}{1-\left(\frac{P-P_0}{P_0}\right)^2}P$$

$$= \frac{4(P-P_0)^2}{2P_0-P} = \frac{4(0.038)^2}{0.036} = 15.2\times10^{-2}$$

When degree of dissociation $\alpha = 0.90$, we have

$$P = K_P\,\frac{(1-\alpha^2)}{4\alpha^2} = 15.2\times10^{-2}\times\frac{(1-0.81)}{4\times0.81} = 8.9\times10^{-2}\text{ atm.}$$

Problem 6. Ammonia in eqm. with 1 : 3 N_2-H_2 mixture at 44 atm and 350°C is 15% by weight. Calculate K_P.

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \rightleftharpoons NH_3$$

100 gm mixture contains 15 gm ammonia, $\frac{14\times85}{17}$ gm N_2 and $\frac{3\times85}{17}$ gm of H_2. Then,

	NH_3	N_2	H_2	Total
in moles	0.88	2.5	7.5	10.88
in pressures	$\frac{0.88\times44}{10.88}$	$\frac{2.5\times44}{10.88}$	$\frac{7.5\times44}{10.88}$	44

$$\therefore \quad K_P = \frac{[0.88\times44/10.88]}{[2.5\times44/10.88]^{\frac{1}{2}}\,[7.5\times44/10.88]^{\frac{3}{2}}} = 6.7\times10^{-3}$$

Problem 7. At 127°C, the eqm. constant K_P for the reaction

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$$

is 2.4 in atmospheres. 6.75 gm of SO_2Cl_2 are placed in an empty 1-litre bulb and the temperature raised to 127°C. What would be the pressure of SO_2, Cl_2 and SO_2Cl_2 gases?

Also calculate the pressure of these gases if the same quantity of SO_2Cl_2 were taken into the bulb already containing chlorine at 1 atm. Compare if the results are consistent with the Le-Chatelier principle.

In absence of dissociation, the initial pressure (P) of SO_2Cl_2 is

$$P\times1 = \frac{6.75}{135}\times0.082\times(273+127),\quad\text{or}\quad P = 1.64\text{ atm.}$$

Now $$K_P = \frac{P_{SO_2}\times P_{Cl_2}}{P_{SO_2Cl_2}} = \frac{P^2_{SO_2}}{P-P_{SO_2}}\quad[\text{ since } P_{SO_2} = P_{Cl_2}\,]$$

$$= \frac{P^2_{SO_2}}{1.64-P_{SO_2}} = 2.4$$

Solving : $P_{SO_2} = P_{Cl_2} = 1.118$ atm, $P_{SO_2Cl_2} = 0.522$ atm.

(*b*) When the bulb already contains chlorine at 1 atm, let the partial pressure of SO_2 at eqm. be π. Then, $P_{Cl_2} = (\pi + 1)$ and $P_{SO_2Cl_2} = 1.64 - \pi$

$$\therefore \qquad K_P = \frac{\pi(\pi+1)}{1.64-\pi} = 2.4$$

Solving : $\pi = 0.912$, *i.e.*, $P_{SO_2} = 0.912$; $P_{Cl_2} = 1.912$; $P_{SO_2Cl_2} =$ 0.728 atm.

14.6. Free Energy Change and Equilibrium Constant : The Reaction Isotherm

The free energy change and the equilibrium constant of a chemical process are related to one another.

Consider a general reaction, $aA + bB \rightleftharpoons dD + eE$

in which suppose at a given temperature T and at a given set of arbitrarily chosen concentrations (or pressures), a moles of A react with b moles of B yielding d moles of D and e moles of E.

The change in the thermodynamic potential in the system due to the chemical reaction at constant temperature and pressure would be,

$$\triangle G = G_{\text{resultants}} - G_{\text{reactants}} = d\mu_D + e\mu_E - a\mu_A - b\mu_B$$

where μ-terms are the respective chemical potentials.

Since $\mu = RT \ln a + z$,

$$\begin{aligned}\triangle G &= d[RT \ln a_D + z_D] + e[RT \ln a_E + z_E] - \\ &\qquad a[RT \ln a_A + z_A] - b[RT \ln a_B + z_B] \\ &= RT \ln \frac{a_D^d \times a_E^e}{a_A^a \times a_B^b} + dz_D + ez_E - az_A - bz_B \\ &= RT \ln \frac{a_D^d \times a_E^e}{a_A^a \times a_B^b} + Z\,(\text{constant})\end{aligned}$$

where a_A, a_B . . . etc. are the activities of the components in the arbitrarily chosen conditions for the reaction.

It would be remembered that this relation is valid for any chosen state and therefore would also be valid if we start with the components in the equilibrium state. Then, using suffix ϵ for denoting equilibrium conditions,

$$\triangle G^{\epsilon} = RT \ln \frac{a_{\epsilon D}^d \times a_{\epsilon E}^e}{a_{\epsilon A}^a \times a_{\epsilon B}^b} + Z = RT \ln K_a + Z$$

But at equilibrium, $\triangle G^{\epsilon} = 0$, hence $Z = -RT\, ln\, K_a$

Then for any chemical reaction, the thermodynamic potential change,

$$\triangle G = -RT\, ln\, K_a + RT\, ln\, \frac{a_D^d \times a_E^e}{a_A^a \times a_B^b}$$

$$= -RT\, ln\, K_a + RT\, \Sigma \nu\, ln\, a \qquad \ldots (14.10)$$

This relation is commonly known as the *reaction isotherm.*

When the systems approach ideality, activities may be replaced by fugacities or pressures or by concentrations. The modified forms of the reaction isotherm would be

$$\left.\begin{aligned} \triangle G_C &= -RT\, ln\, K_C + RT\Sigma \nu\, ln\, C \\ \triangle G_P &= -RT\, ln\, K_P + RT\Sigma \nu\, ln\, P \end{aligned}\right\} \qquad \ldots (14.11)$$

The standard states chosen in each case must be specified.

The importance of the isotherm lies in the fact that it can predict in which way a reaction, in a given set of conditions, would proceed. In eqn. (14.11), if the arbitrarily chosen concentrations $\Sigma \nu\, ln\, C$ is less than $ln\, K_C$, $\triangle G$ is $-ve$, a spontaneous reaction would take place. If $\Sigma \nu\, ln\, C$ be greater than $ln\, K_C$, the reaction will not occur. In that case if we reduce the concentrations of resultants and increase those of reactants, the possibility of reaction in the desired direction would improve. It is thus that thermodynamics provides us the clue to the knowledge of conditions favouring a chemical process.

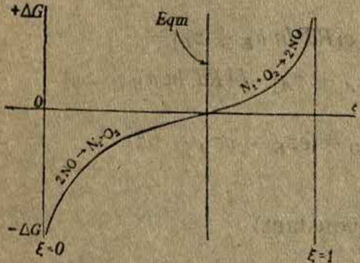

Fig. 14*a*. $\triangle G$ versus ξ, the extent of reaction

This behaviour can be schematically represented as in Fig. 14*a*, where $\triangle G$ is plotted against the extent of reaction (ξ). The criterion for eqm. is $\triangle G = 0$. To the right of the eqm. $\triangle G = +ve$, the opposite process will be favoured. To the left of the eqm. $\triangle G$ is $-ve$, hence the desired process is spontaneous.

Now $\quad \triangle G = -RT\, ln\, K_a + RT\Sigma \nu\, ln\, a$

If the reaction is carried out in such conditions that every reactant and resultant be maintained at unit activities, *i.e.*, all the reactants and resultants are in standard states, then $\Sigma \nu \ln a = 0$. So,

$$\triangle G^0 = -RT \ln K_a \qquad \ldots (14.12)$$

where $\triangle G^0$ is the standard free energy change accompanying conversion of reactants in standard states to resultants in their standard states. The eqm. constant is thus a measure of the free energy change of the process.

Rewriting eqn. 14.10 ; $\triangle G = \triangle G^0 + RT \Sigma \nu \ln a$

$$\ldots (14.13)$$

As before, for ideally behaving systems,

$$\left.\begin{array}{ll} (i) & \triangle G = \triangle G^0 + RT \Sigma \nu \ln P \\ (ii) & \triangle G = \triangle G^0 + RT \Sigma \nu \ln C \end{array}\right\} \qquad \ldots (14.14)$$

Further, for changes in standard states,

$$\left.\begin{array}{l} \triangle G^0 = -RT \ln K_p \\ \triangle G^0 = -RT \ln K_c \end{array}\right\} \qquad \ldots (14.15)$$

(the standard states should be specified in each case)

These relations are of unique importance to the chemist.

The knowledge of $\triangle G^\circ$ would therefore allow the evaluation of the eqm. constant K_P or K_C . Alternatively, from the experimental values of eqm. constants, the standard free energy change can be computed.

Since $\triangle G^\circ = -RT \ln K$ (K, the appropriate eqm. constant)

hence $K = e^{-\triangle G^\circ / RT}$ . . . (14.16)

Now $\triangle G^0 = \triangle H^0 - T \triangle S^0$, hence $K = e^{\frac{-\triangle H^\circ}{RT}} . e^{\frac{\triangle S^\circ}{R}}$ . . . (14.17)

It is evident that

(*i*) When $\triangle G^0 < 0$, *i.e.*, $\triangle G$ is negative, K will be greater than unity. As $\triangle G^0$ becomes more and more negative, K will be larger and larger.

(*ii*) The more negative the value of $\triangle H^0$, the larger will be the value of K.

The higher values of K indicate greater extent of reaction to produce the resultants. The reaction will be favoured by negative values of $\triangle H^0$ and $\triangle G^0$ and by increase of randomness *i.e.*, positive values of $\triangle S^0$.

Problem 8. At 1000°K, the value of K_P for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, is 3.5. What would be the thermodynamic potential change if 2 moles of

SO_3 at 1 atm are formed from SO_2 at 0.1 atm and O_2 at 0.2 atm at this temperature ? [Use R in litre-atm.]

$$\Delta G = -RT\,ln\,K_P + RT\,ln\frac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}}$$

$$= -RT\,ln\,3.5 + RT\,ln\frac{(1)^2}{(0.1)^2 \times (0.2)} = 9890 \text{ cal}$$

Problem 9. For the reaction, $H_2 + S \rightleftharpoons H_2S$, calculate K_P at 25°C if the standard thermodynamic potential of H_2S is -7.88 Kcal.

We have $$\Delta G^0 = \left[\Delta G^0{}_f\right]_{H_2S} - \left[\Delta G^0{}_f\right]_{H_2} - \left[\Delta G^0{}_f\right]_S$$

$$= -7880 \qquad -0 \qquad -0$$

$$= -7880 \text{ cal}$$

Hence $$\log K = -\frac{\Delta G^0}{2.3RT} = \frac{7880}{2.3 \times (1.98)(298)} = 5.78$$

$$\therefore \quad K = 6.02 \times 10^5$$

Problem 10. Calculate K_P , for the water-gas reaction, $CO + H_2O \rightleftharpoons CO_2 + H_2$, at 25°C. [Use standard thermodynamic potential tables.]

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$\Delta G^0{}_f : -32.8 \quad -54.64 \quad -94.26 \quad 0$$

$$\therefore \Delta G^0 = \Sigma \Delta G^0{}_f = -94.26 + 0 - (-32.8) - (-54.64) = -6.82 \text{ Kcal}$$

$$\log K_P = -\frac{-6820}{2.3 \times (1.98)(298)} = 5.025 \;;\; \text{or } K_P = 1.06 \times 10^5$$

ΔG^0 can be evaluated from standard heat of reaction ΔH^0 and the entropy change ΔS^0 (from entropies of the entities from the Third Law). We can then utilise eqn. (14.15) to obtain K_P.

Problem 11. The heat of formation of ammonia (NH_3) at 25°C is -11.04 Kcal. Calculate K_P using standard entropy table given in Section 8.5.

In the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$; $\qquad \Delta H^0 = -11040$ cal

Entropy, $(S^0) \rightarrow \frac{1}{2}(45.7) \quad \frac{3}{2}(3.12) \quad , 46 \qquad$ *i.e.*, $\Delta S^0 = -23.7$ e.u.

$$\therefore \quad \Delta G^0 = \Delta H^0 - T\Delta S^0 = -11040 - (298)(-23.7) = -3978 \text{ cal}$$

Now $$\log K_P = \frac{-\Delta G^0}{2.3\,RT} = \frac{3978}{2.3 \times 1.98 \times 298} = 2.932$$

or $K_P = 8.5 \times 10^2$ at 25°C.

14.7. Pressure dependence of Equilibrium Constant

At a given temperature K_P and K_C are independent of pressure but K_x depends upon pressure ; from (14.9),

$$K_x = K_P \, . P^{-\triangle \nu}$$

or
$$\ln K_x = - \triangle \nu \ln P + C \text{ (constant)}$$

or
$$\left[\frac{d \ln K_x}{dP}\right]_T = \frac{- \triangle \nu}{P} = \frac{- \triangle V}{RT} \qquad \ldots (14.18)$$

In a reaction where $\triangle \nu = 0$, K_x also will remain unaffected with change in pressure. If $\triangle \nu$ is $+ ve$, as in the dissociation of PCl_5, $\ln K_x$ will decrease with increase in pressure. Hence degree of dissociation shall decrease.

If $\triangle \nu$ is $- ve$, as in the formation of ammonia, $\ln K_x$ will increase with pressure ; hence more of ammonia will be formed.

14.8. Temperature dependence of Equlibrium Constant. van't Hoff Equation

At a given temperature, the eqm. constant of a reaction remains unaltered, but its magnitude varies considerably when the temperature is changed. This will be evident from the results recorded below:

TABLE : EQUILIBRIUM CONSTANTS AT DIFFERENT TEMPERATURES

Reaction : $N_2+O_2 \rightleftharpoons 2NO$		$H_2S \rightleftharpoons H_2+S$		$Cl_2 \rightleftharpoons 2Cl$	
Temp. (°K)	$K_P \times 10^4$	*Temp.* (°K)	$K_P \times 10^4$	*Temp.* (°K)	K_P
2000	4.08	750	0.91	800	1.04×10^{-10}
2200	11.00	830	3.8	1200	2.48×10^{-5}
2400	25.10	1065	11.8	1600	1.29×10^{-3}
2600	50.30	1132	26.0	2000	5.70×10^{2}

A quantitative expression for the variation of eqm. constant with temperature can easily be deduced.

The reaction isotherm : $\triangle G = -RT \ln K_P + RT \Sigma \nu \ln P$

Differentiating with respect to temperature at *constant pressure*,

$$\frac{d(\triangle G)}{dT} = - RT \frac{d \ln K_P}{dT} - R \ln K_P + RT \frac{d\Sigma \nu \ln P}{dT} + R\Sigma \nu \ln P$$

The term $\Sigma \nu \ln P$ is a fixed quantity containing arbitrarily chosen pressures of the components, hence $\frac{d\Sigma \nu \ln P}{dT} = 0$.

Multiplying both sides by T,

$$T\frac{d(\triangle G)}{dT} = -RT^2\frac{d \ln K_P}{dT} - RT \ln K_P + RT\Sigma \nu \ln P$$

$$= -RT^2\frac{d \ln K_P}{dT} + \triangle G$$

Hence, $$RT^2\frac{d \ln K_P}{dT} = \triangle G - T\frac{d(\triangle G)}{dT} \qquad \ldots (14.19)$$

But from Gibbs-Helmholtz equation, $\triangle G - T\frac{d(\triangle G)}{dT} = \triangle H$, where $\triangle H$ is the heat-change (*i.e.*, heat of reaction) at temperature T.

$$\therefore \quad RT^2\frac{d \ln K_P}{dT} = \triangle H$$

$$\therefore \quad \frac{d \ln K_P}{dT} = \frac{\triangle H}{RT^2} \qquad \ldots (14.20)$$

This is commonly known as the **van't Hoff equation**, which gives the variation of K_P with temperature T.

We know further, $$K_P = K_C (RT)^{\triangle \nu}$$

or, $$\ln K_P = \ln K_C + \triangle \nu \ln R + \triangle \nu \ln T$$

or $$\frac{d \ln K_P}{dT} = \frac{d \ln K_C}{dT} + \frac{\triangle \nu}{T}$$

Substituting this in the equation above (at const. pressure),

$$\frac{d \ln K_C}{dT} = \frac{\triangle H}{RT^2} - \frac{\triangle \nu}{T} = \frac{\triangle H - \triangle \nu RT}{RT^2} = \frac{\triangle H - P\triangle v}{RT^2}$$

or $$\frac{d \ln K_C}{dT} = \frac{\triangle U}{RT^2} \qquad \ldots (14.21)$$

where $\triangle U$ is the energy-change at constant volume, *i.e.*, heat-change at constant volume. This relation for the variation of equilibrium constant K_C with temperature at constant volume is often mentioned as **van't Hoff isochore.**

14.9. The Integration of the van't Hoff Equation

The integration of the van't Hoff equation (14.20) would enable us to calculate numerically the shift of the equilibrium-constant with temperature.

$$\text{Now,} \quad \int d\,ln\,K_P = \frac{\triangle H}{R}\int\frac{dT}{T^2} \quad \text{(assuming } \triangle H \text{ as constant)}$$

$$\text{or} \qquad ln\,K_P = -\frac{\triangle H}{R}.\frac{1}{T} + C'\,\text{(constant)} \qquad \ldots (14.22)$$

Integrating between two temperatures, T_1 and T_2, such that $T_1 > T_2$, we have,

$$ln\,\frac{K_{P_1}}{K_{P_2}} = -\frac{\triangle H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{\triangle H}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right] \quad \ldots (14.23)$$

If the reaction be exothermic, *i.e.*, $\triangle H$ is $-$ *ve*, then the expression on the right-hand is negative, hence $K_{P_1} < K_{P_2}$. It means that with rise of temperature, K_P will diminish, *i.e.*, resultants (at equilibrium) would be less. In other words, exothermic reactions are not favoured by rise of temperatures. If the reaction be endothermic, $K_{P_1} > K_{P_2}$ *i.e.*, endothermic reactions would be favoured by rise in temperature.

$$\text{From eqn. 14.22 ;} \qquad \log K_P = -\frac{\triangle H}{2.303\,R}.\frac{1}{T} + \text{constant} \qquad \ldots (14.24)$$

A plot of log K_P against $\frac{1}{T}$ would be linear, and the slope of the curve will give the value of $\triangle H$, as illustrated in Fig. 14*b*.

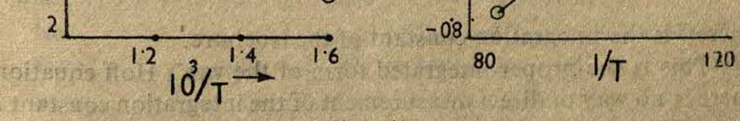

Fig. 14*b*

(*a*) $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$ (endothermic)

(*b*) $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ (exothermic)

If $\triangle H$, the heat of reaction, be very small, *i.e.*, $\triangle H \rightarrow 0$, as in the reaction between ethyl alcohol and acetic acid, $ln\ K$ = constant, *i.e.*, eqm. constant does not change with temperature.

Problem 12. The dissociation constant of $CaCO_3$ at 900°C and 1000°C are 790 mm and 2940 mm. Calculate the heat of dissociation at this temperature-range.

$$CaCO_3 = CaO + CO_2$$

$$K_a = \frac{a_{CaO} \times a_{CO_2}}{a_{CaCO_3}} = a_{CO_2}, \text{ hence } K_P = P_{CO_2} = P \text{ (say)}$$

Then $$ln\ \frac{K_P}{K_P'} = ln\ \frac{P}{P'} = -\frac{\triangle H}{R}\left[\frac{1}{T} - \frac{1}{T'}\right]$$

i.e., $$ln\ \frac{790}{2940} = -\frac{\triangle H}{2}\left[\frac{1}{1173} - \frac{1}{1273}\right] \text{ or } \triangle H = 39646 \text{ cal}$$

The relation (14.24) is only an approximate one as $\triangle H$ has been assumed constant. It is known that $\triangle H$ often varies considerably with temperature. A proper integration of the van't Hoff equation may now be attempted.

Consider the reaction, $aA + bB \rightleftharpoons dD + eE$

Now from Kirchhoff's equation (Sec. 2.9),

$$\left[\frac{\partial(\triangle H)}{\partial T}\right]_P = \triangle C_P = C_{P_{resultant}} - C_{P_{reactant}}$$

or $$\triangle H_T - \triangle H_0 = aT + \frac{\beta T^2}{2} + \frac{\gamma T^3}{3} + \cdots$$

The van't Hoff equation will then be

$$\frac{d\ ln\ K_P}{dT} = \frac{\triangle H_T}{RT^2} = \frac{\triangle H_0}{RT^2} + \frac{a}{RT} + \frac{\beta}{2R} + \frac{\gamma T}{3R} + \cdots$$

or $$ln\ K_P = -\frac{\triangle H_0}{RT} + \frac{a}{R} ln\ T + \frac{\beta T}{2R} + \frac{\gamma T^2}{6R} + \ldots I \quad \ldots (14.25)$$

where I is the integration constant of the isochore.

This is the proper integrated form of the van't Hoff equation. There is no way of direct measurement of the integration constant I. As such the evaluation of K_P from this relation proves difficult.

The constants $a, \beta, \gamma, \ldots$ etc. are available from direct measurements of heat capacities of the reactants and resultants at different temperatures. If $\triangle H_T$, the heat of reaction, is also determined at different temperatures, we can find $\triangle H_0$. Thus, thermal measurements give us the constants on the right-hand side of equation (14.25) except 'I'.

In those cases, when K_P can be experimentally determined, the value of I will be at once available from this equation.

Rewriting equation (14.25),

$$R \ln K_P = -\frac{\triangle H_0}{T} + \alpha \ln T + \frac{\beta}{2}T + \frac{\gamma}{6}T^2 \ldots + IR$$

$$= -\frac{\triangle H_0}{T} + A + IR$$

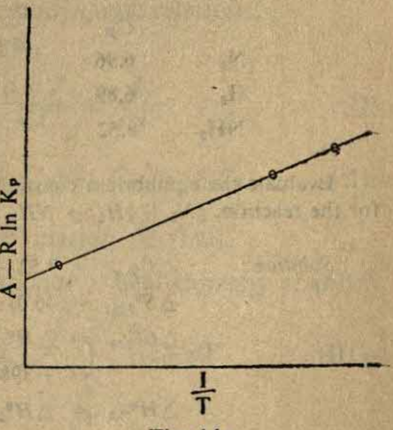

Fig. 14c
Determination of I and $\triangle H_0$

where $A = \alpha \ln T + \frac{\beta}{2} T + \frac{\gamma}{6} T^2 + \ldots$

such that 'A' is a function of temperature only for any given reaction.

That is, $A - R \ln K_P = \frac{\triangle H_0}{T} - IR$ . . . (14.26)

If we plot $(A - R \ln K_P)$ against $1/T$, the slope of the straight line would lead to the value of $\triangle H_0$ (heat change at absolute zero) and the intercept IR. Thus, both I and $\triangle H_0$ can be obtained (Fig. 14.c).

Problem 13. Given $C_{P_{H_2}} = 6.5 + 0.0009T$; $C_{P_{Br_2}} = 7.4 + 0.001T$,

$$C_{P_{HBr}} = 6.5 + 0.001T.$$

Write down an expression for $\triangle G^0$ for the reaction, $\frac{1}{2}H_2 + \frac{1}{2}Br_2 = HBr$, in which $\log K_P = 2.44$ at 1381°K and $\triangle H_0 = -11970$ cal.

Now, $\triangle C_P = C_{P_{HBr}} - \frac{1}{2}C_{P_{H_2}} - \frac{1}{2}C_{P_{Br_2}} = -0.45 + 0.00005T$

Since $\triangle C_P = \alpha + \beta T$, we have $\alpha = -0.45$, $\beta = +0.00005$

Again $\log K_P = 2.44$, *i.e.*, $\ln K_P = 5.62$

And $\ln K_P = \frac{-\triangle H_0}{RT} + \frac{\alpha}{R} \ln T + \frac{\beta}{2R} T + I$,

(see equation 14.25)

or
$$5.62 = \frac{11970}{2\times1381} + \frac{(-.45)}{2}\times2.303 \log 1381 + \frac{0.00005}{4} \times 1381 + I$$

whence
$$I = 2.9$$

$$\therefore \quad \Delta G^0 = -RT \ln K_P = \Delta H_0 - aT \ln T - \frac{\beta}{2}T^2 - IRT$$
$$= -11970 + 0.45T \ln T - 0.000025T^2 - 5.8T$$

Problem 14. The standard heat capacity, entropy and enthalpy of formation are given in cal/mole at 1 atm and 298°K for nitrogen, hydrogen and ammonia :

	C_p	S^0	ΔH^0
N_2	6.96	45.76	—
H_2	6.89	31.20	—
NH_3	8.52	46.01	−11040

Evaluate the equilibrium constant at 298°K and 773°K. for the reaction, $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$.

Solution :
$$\Delta C_p = 8.52 - \tfrac{1}{2}(6.96) - \tfrac{3}{2}(6.89) = -5.29 \text{ cal}$$
$$\Delta S^0_{298} = 46.01 - \tfrac{1}{2}(45.76) - \tfrac{3}{2}(31.21) = -23.69 \text{ cal/°K}$$
$$\Delta G^0_{298} = \Delta H^0 - T\Delta S^0 = -11040 - (298)(-23.69)$$
$$= -3980 \text{ cal}$$
$$\Delta H^0_{773} = \Delta H^0_{298} + \Delta C_p(773-298) = -11040 + (-5.29)475$$
$$= -13540 \text{ cal (assuming } \Delta C_p \text{ remains unaltered)}$$

$$\therefore \log K_{298} = \frac{-\Delta G^0_{298}}{2.303RT} = \frac{3980}{2.303\times2\times298} \approx 2.92$$

$$\text{or} \quad K_{298} = 8.3\times10^2$$

Using eqn (14.25), $d \ln K_T = \dfrac{\Delta H^0_{298} + \Delta C_P\,(T-298)}{RT^2}\,dT$

$$= \frac{\Delta H^0_{298} - 298\,\Delta C_p}{RT}\,dT + \frac{\Delta C_p}{RT}\,dT$$

$$\therefore \quad \int_{K_{298}}^{K_{773}} d \ln K = \frac{\Delta H^0_{298} - 298\,\Delta C_p}{R}\int_{298}^{773}\frac{dT}{T^2} + \frac{\Delta C_p}{R}\int_{298}^{773}\frac{dT}{T}$$

or
$$\ln K_{773} - \ln K_{298} = -\frac{\Delta H^0_{298} - 298\,\Delta C_p}{R}\left(\frac{1}{773} - \frac{1}{298}\right) + \frac{\Delta C_p}{R}\ln\frac{773}{298}$$

or $$2.303[\log K_{773}-\log K_{298}] = -\frac{-11040-298(-5.29)}{2}\left(\frac{1}{773}-\frac{1}{298}\right) - \frac{5.29\times 2.303}{2}\log\frac{773}{298}$$

or $$\log K_{773}-2.92 = \frac{9465}{4.60}\left[\frac{1}{773}-\frac{1}{298}\right] - 2.65\log_{773}+2.65\ \log 298$$

or $\log K_{773} = -2.44$; *i.e.*, $K_{773} = 3.6\times 10^{-3}$

14.10. Computation of Eqm. Constant (K_P) of a gaseous reaction

The equilibrium constant of a gaseous reaction can be evaluated with the help of some common thermodynamic relations.

For a solid subliming into a gas,

(*a*) Clausius Clapeyron Eqn : $\frac{d\ln P}{dT} = \frac{L_s}{RT^2}$ ... (I)

(*b*) Kirchhoff equation : $\frac{dL_s}{dT} = C_{P_g} - C_{P_s} = \triangle C_P'$ ... (II)

L_s = latent-heat of sublimation per mole

$\triangle C_P'$ = heat-capacity of vapour − heat-capacity of solid

From (II), $$L_S = L_{S0} + \int_0^T \triangle C_P' dT \qquad \text{... (III)}$$

From (I) and (III), $$\frac{d\ln P}{dT} = \frac{L_{S0} + \int_0^T \triangle C_P' dT}{RT^2}$$

or $$\ln P = -\frac{L_{S0}}{RT} + \int \frac{\int_0^T \triangle C_P' dT}{RT^2} dT + i \qquad \text{... (IV)}$$

where i = chemical constant (see Sec. 13.6).

But $$\int \frac{\int_0^T \triangle C_P' dT}{RT^2} dT = -\frac{\int_0^T \triangle C_P' dT}{RT} + \int_0^T \frac{\triangle C_P'}{RT} dT$$

(from III). $$= \frac{L_{S0} - L_S}{RT} + \int_0^T \frac{\triangle C_P'}{RT} dT \qquad \text{... (V)}$$

Substituting this in equation (IV),

$$\ln P = -\frac{L_S}{RT} + \int_0^T \frac{\triangle C_P' dT}{RT} + i \qquad \ldots (VI)$$

Now, consider a chemical reaction, *in the gas phase*,

$$m_A A + m_B B \rightleftharpoons m_C C + m_D D,$$

in which, obviously,

$$K_P = \frac{(P_C)^{m_C} (P_D)^{m_D}}{(P_A)^{m_A} (P_B)^{m_B}} \quad (P\text{-terms are partial pressures})$$

and further

$$\frac{d \ln K_P}{dT} = \frac{\triangle H^G}{RT^2}$$

The superscript G will be used for gaseous state and S for solid state. $\triangle H^G$ is thus the heat of reaction in the gaseous state.

This van't Hoff equation is similar to that of Clausius-Clapeyron equation. By following the same steps as in the equations (I—VI), we can write

$$\ln K_P = -\frac{\triangle H^G}{RT} + \int_0^T \frac{\triangle C_P^G}{RT} dT + I \qquad \ldots (VII)$$

where I is the integration constant of the van't Hoff equation.

From Kirchhoff equation, we can say,

$$\frac{\partial(\triangle H^G)}{\partial T} = \triangle C_P^G = m_C C_{P_C}^G + m_D C_{P_D}^G - m_A C_{P_A}^G - m_B C_{P_B}^G$$

where C_P^G -terms are the respective heat-capacities in the gaseous state.

Let us now consider the same chemical reaction carried out in the solid state at the same temperature, that is

$$m_A A^S + m_B B^S \rightleftharpoons m_C C^S + m_D D^S$$

We may imagine that the solid reactants are first vaporised and after the reaction, the resultants are condensed back to the solid state, the thermodynamic potential change would then be given by (vapours assumed to behave ideally),

$$\triangle G^S = RT\ln\frac{P_A^{m_A}\times P_B^{m_B}}{P_A^{0m_A}\times P_B^{0m_B}} - RT\ln\frac{P_C^{m_C}\times P_D^{m_D}}{P_C^{0m_C}\times P_D^{0m_D}},$$

$$= RT\ln\frac{P_C^{0m_C}\times P_D^{0m_D}}{P_A^{0m_C}\times P_B^{0m_B}} - RT\ln\frac{P_C^{m_C}\times P_D^{m_D}}{P_A^{m_A}\times P_B^{m_B}}$$

$$= RT\ln\frac{P_C^{0m_C}\times P_D^{0m_D}}{P_A^{0m_A}\times P_B^{0m_B}} - RT\ln K_P$$

where P^0-terms are the vapour pressures of the solids and P-terms are the equilibrium partial vapour pressures.

$$\text{or, } \triangle G^S = -RT\ln K_P + RT\,[m_C\ln P_C^\circ + m_D\ln P_D^\circ - m_A\ln P_A^\circ - m_B\ln P_B^\circ] \qquad \ldots\text{(VIII)}$$

Substituting (VI) and (VII) in this equation (VIII), we find

$$\triangle G^S = -RT\left[-\frac{\triangle H^G}{RT} + \int_0^T \frac{\triangle C_P^G}{RT}\,dT + I\right]$$

$$+ RT\left\{m_C\left[-\frac{L_{S_C}}{RT} + \int_0^T \frac{\triangle C'_{P_C}}{RT}\,dT + i_C\right]\right.$$

$$+ m_D\left[-\frac{L_{S_D}}{RT} + \int_0^T \frac{\triangle C'_{P_D}}{RT}\,dT + i_C\right]$$

$$- m_A\left[-\frac{L_{S_A}}{RT} + \int_0^T \frac{\triangle C'_{P_A}}{RT}\,dT + i_A\right]$$

$$\left.- m_B\left[-\frac{L_{S_B}}{RT} + \int_0^T \frac{\triangle C'_{P_B}}{RT}\,dT + i_B\right]\right\}$$

Simplifying,

$$\triangle G^S = [m_A L_{S_A} + m_B L_{S_B} - m_C L_{S_C} - m_D L_{S_D} + \triangle H^G]$$

$$+ RT\int_0^T\left(\frac{m_C\triangle C'_{P_C} + m_D\triangle C'_{P_D} - m_A\triangle C'_{P_A} - m_B\triangle C'_{P_B} - \triangle C_P^G}{RT}\right)dT$$

$$+ RT[m_C i_C + m_D i_D - m_A i_A - m_B i_B - I] \qquad \ldots\text{(IX)}$$

It is to be noted that in the right-hand side

(*a*) the terms in the first paranthesis is the change in the heat-content for the reaction in the solid state $= \triangle H^S$

(*b*) the numerator of the integrand is the difference of heat capacities of resultants and reactants in the solid state $= -\triangle C_P^S$ The equation (IX) can then be written as,

$$\triangle G^S = \triangle H^S - T\int_0^T \frac{\triangle C_P^S}{T}\,dT + RT\,(\Sigma vi - I) \qquad \ldots (X)$$

On the other hand, the Gibbs-Helmholtz relation for the reaction in the solid state may be written as

$$\triangle G^S = \triangle H^S - T\int_0^T \frac{\triangle C_P^S}{T}\,dT \qquad \ldots (XI)$$

Comparing equations (X) and (XI)

$$\Sigma vi - I = 0 \quad \text{or} \quad I = \Sigma vi$$

From equation (VII), then

$$\ln K_P = -\frac{\triangle H^G}{RT} + \int_0^T \frac{\triangle C_P^G}{RT}\,dT + \Sigma vi \qquad \ldots (XII)$$

In equation (XII), Σvi is the algebraic sum of the chemical constants and may be replaced by $\triangle S_0/R$, from equation (13.20).

$$\therefore\ \ln K_p = \frac{-\triangle H^G}{RT} + \int_0^T \frac{\triangle C_P^G}{RT}\,dT + \frac{\triangle S_0}{R} \qquad \ldots (XIII)$$

This is called the *Nernst's equation.*

Prof. M. N. Saha made use of this equation in the study of the thermal ionisation of monatomic vapours such as those of metals at very high temperatures. The ionisation may be represented as

$$M \rightleftharpoons M^+ + e$$

$1-\alpha \quad \alpha \quad \alpha = 1+\alpha$; ($\alpha$ = degree of dissociation).

The eqm. constant, $K_P = \alpha^2 P/(1-\alpha^2)$

Assuming atoms, ions and electrons behaving as monatomic gases, C_p for each is $5/2\ R$, hence $\triangle C_p = 5/2\ R$ (for the process).

Again, the heat of dissociation $\triangle H^G = N_0 FE$, where E= ionisation potential of an atom in volts.

$$\therefore\quad \triangle H^G = [6.06 \times 10^{23} \times 1.59 \times 10^{-19}.E]/4.2$$

$$= 23070\ E\ \text{cal/mole}$$

Substituting these in eqn. XIII,

$$\ln\left(\frac{\alpha^2 P}{1-\alpha^2}\right) = -\frac{23070\,E}{RT} + \tfrac{5}{2}\ln T + \frac{\triangle S_0}{R}$$

or

$$\log\frac{\alpha^2 P}{1-\alpha^2} = \frac{-23070}{4.60}\cdot\frac{E}{T} + \tfrac{5}{2}\log T + \frac{\triangle S_0}{4.60}$$

From a statistical computation of entropies of the components it was shown that

$$\triangle S_0/R = \log\frac{g_i g_e}{g_a} - 6.49$$

where g_i, g_e and g_a are the weight factors of ions, electrons and atoms. The pressure is expressed in atmospheres.

$$\log\frac{\alpha^2 P}{1-\alpha^2} = -5050\,E/T + \tfrac{5}{2}\log T + \log(g_i g_e/g_a) - 6.49 \quad \ldots \text{(XIV)}$$

In the ionisation of sodium vapour, $g_{\mathrm{Na}+} = 1$, $g_e = 2$, $g_{\mathrm{Na}} = 2$ and $E = 5.12$ volts. By comparing the intensities of the spectral lines from atoms and from ions, α, the degree of ionisation, was measured. With a given pressure, the temperature could be calculated from eqn. (XIV). In fact, Saha employed this in estimating stellar temperatures. Taking a star as a spherical mass of blazing vapours, the pressure could be computed, the differential intensities in the spectral studies of the same atom and its ions gave α. Other values being known, the temperature was obtained.

14.11 Equlibrium Constant from Partition Function

The eqm. constant of a reaction is related to the Gibb's free energy change by the relation

$$\triangle G^0 = -RT\ln K_p$$

On the other hand, the Gibb's free energy can be expressed in terms of partition functions (eqn. 11.39)

$$G = -RT\,ln\,(f/N) \quad \ldots (a)$$

It is hence possible to predict the value of eqm. constant from a knowledge of the partition functions of the participating components.

The total energy of a molecule,

$$\epsilon = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec} + \epsilon_0$$

where ϵ_0 is the zero-energy, *i.e.*, the energy possessed by the molecule at the ground state at $T = 0°\text{K}$. Usually the zero of energy to which all other energies are referred is the energy of dissociated atoms infinite distance apart, at $T = 0°\text{K}$. The molecule at 0°K would possess some energy, which is the zero-energy, ϵ_0.

The molecular partition function of a gas is then

$$f^0 = f^0{}_{tr} \times f^0{}_{rot} \times f^0{}_{vib} \times f^0{}_{elec} \times e^{-\epsilon_0/kT}$$

or $$f^0 = \frac{(2\pi mkT)^{3/2}}{h^3} V \times f^0{}_{int} \times \phi_0$$

where $\phi_0 = e^{-\epsilon_0/kT}$ and $f^0{}_{int} = f^0{}_{rot} \times f^0{}_{vib} \times f^0{}_{elec}$

Putting $\frac{(2\pi mkT)^{3/2}}{h^3} f^0{}_{int} = f'$, we may write

$$f^0 = f' V \phi_0$$

Substituting this in (*a*) above, $G = -RT \ln \left(\frac{f' V \phi_0}{N}\right)$

At the standard state, where $P = 1$, we have

$$G^0 = -RT \ln \frac{f' RT}{N} \phi_0 = -RT \ln (f' kT \phi_0) \qquad \ldots (b)$$

Let us now consider a gaseous reaction,

$$aA + bB \rightleftharpoons cC + dD$$

in which $$\triangle G^0 = cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B$$

$\therefore$ From (*b*) above, $\triangle G^\circ = -RT \ln \left[\frac{f'^c_C \times f'^d_D}{f'^a_A \times f'^b_B} (kT)^{\triangle n} \phi_0{}^{\triangle n}\right]$

where $$\triangle n = (c + d) - (a + b)$$

and $$\phi_0^{\triangle n} = \frac{\phi_{0C}^c \times \phi_{0D}^d}{\phi_{0A}^a \times \phi_{0B}^b}$$

But, $$\triangle G^0 = -RT \ln K_P$$

Hence, the eqm. constant,

$$K_P = \frac{f'^{\,c}_{C} \times f'^{\,d}_{D}}{f'^{\,a}_{A} \times f'^{\,b}_{B}} \times \phi_0^{\triangle n} \times (kT)^{\triangle n}$$

$$= \frac{f'^{\,c}_{C} \times f'^{\,d}_{D}}{f'^{\,a}_{A} \times f'^{\,b}_{B}} \times e^{-\triangle \epsilon_0 / kT^*} \times (kT)^{\triangle n} \quad \ldots (14.27)$$

We may illustrate this with a few simple examples.

(*i*) Consider the dissociation equilibrium, $I_2 \rightleftharpoons 2I$, in which the eqm. constant can be statistically expressed as

$$K_P = \frac{f_I^2}{f_{I_2}} (kT)\, e^{-\triangle E_0/RT} = \frac{f_{I\,(tr)}^2}{(f_{tr} \cdot f_{vib} \cdot f_{rot} \cdot f_{elec})_{I_2}} \times (kT)(e^{-\triangle E_0/RT})$$

$$= \frac{[g_I (2\pi m_I kT)^{3/2}/h^3]^2\, [kT] e^{-\triangle E_0 RT}}{g_{I_2} [(2\pi m_{I_2} kT)^{3/2}/h^3][8\pi^2 IKT/\sigma h^2] e^{-\frac{1}{2}h\nu/kT} (1 - e^{-h\nu/kT})^{-1}}$$

$$= \frac{g^2{}_I}{g_{I_2}} \cdot \frac{(\pi m_I kT)^{3/2}}{4\pi^2 Ih} (1 - e^{-h\nu/kT})\, e^{\frac{1}{2}h\nu/kT} \cdot e^{-\triangle E_0/RT}$$

where g_I, g_{I_2} are the statistical weight factors, $\sigma = 2$, $m_{I_2} = 2m_I$ and all the entities are supposed to be in their ground states. The magnitudes of I, ν and $\triangle E_0$ are all determinable from spectroscopic measurements. The equilibrium constant can thus be obtained in terms of spectroscopic constants only.

(*ii*) Let us next consider the ionisation of sodium vapour.

$$Na \rightleftharpoons Na^+ + \theta$$

From equation (14.27), $\quad K_P = \dfrac{f_{Na^+} f_\theta}{f_{Na}}\, kT\, e^{-\triangle E_0/RT}$

In this case, only the translational motion is concerned, hence

$$K_P = \frac{g_{Na^+} . g_\theta}{g_{Na}} \frac{[(2\pi m_+ kT)^{3/2}/h^3]\; [(2\pi m_\theta kT)^{3/2}/h^3]}{[(2\pi m_{Na} kT)^{3/2}/h^3]} \times (kT) e^{-\triangle E_0/RT}$$

$$= \frac{g_{Na^+} . g_\theta}{g_{Na}} \frac{(2\pi m_\theta kT)^{3/2}}{h^3} (kT)\, e^{-\triangle E_0/RT}$$

$$^*\phi_0^{\triangle n} = \phi_{0\,C}^{\,c} \times \phi_{0\,D}^{\,d} / \phi_{0\,A}^{\,a} \cdot \phi_{0\,B}^{\,b} = e^{-[c\epsilon_{0C} + d\epsilon_{0D} - a\epsilon_{0A} - b\epsilon_{0B}]/kT}$$

$$= e^{-\triangle \epsilon_0/kT} = e^{-\triangle E_0/RT}$$

where ϵ_0 is the zero-energy, *i.e.*, the energy possessed by the molecule at the ground state at $T = 0°K$. Usually the zero of energy to which all other energies are referred is the energy of dissociated atoms infinite distance apart, at $T = 0°K$. The molecule at 0°K would possess some energy, which is the zero-energy, ϵ_0.

The molecular partition function of a gas is then

$$f^0 = f^0{}_{tr} \times f^0{}_{rot} \times f^0{}_{vib} \times f^0{}_{elec} \times e^{-\epsilon_0/kT}$$

or
$$f^0 = \frac{(2\pi mkT)^{3/2}}{h^3} V \times f^0{}_{int} \times \phi_0$$

where
$$\phi_0 = e^{-\epsilon_0/kT} \text{ and } f^0{}_{int} = f^0{}_{rot} \times f^0{}_{vib} \times f^0{}_{elec}$$

Putting
$$\frac{(2\pi mkT)^{3/2}}{h^3} f^0{}_{int} = f', \text{ we may write}$$

$$f^0 = f' V \phi_0$$

Substituting this in (*a*) above, $G = -RT \ln \left(\frac{f' V \phi_0}{N} \right)$

At the standard state, where $P = 1$, we have

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in which
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$\therefore$ From (*b*) above, $\triangle G^\circ = -RT \ln \left[\frac{f'^c_C \times f'^d_D}{f'^a_A \times f'^b_B} (kT)^{\triangle n} \phi_0{}^{\triangle n} \right]$

where
$$\triangle n = (c + d) - (a + b)$$

and
$$\phi_0^{\triangle n} = \frac{\phi_{0C}^{\,c} \times \phi_{0D}^{\,d}}{\phi_{0A}^{\,a} \times \phi_{0B}^{\,b}}$$

But,
$$\triangle G^0 = -RT\, ln\, K_P$$

Hence, the eqm. constant,

$$K_P = \frac{f'^{\,c}_{C} \times f'^{\,d}_{D}}{f'^{\,a}_{A} \times f'^{\,b}_{B}} \times \phi_0^{\triangle n} \times (kT)^{\triangle n}$$

$$= \frac{f'^{\,c}_{C} \times f'^{\,d}_{D}}{f'^{\,a}_{A} \times f'^{\,b}_{B}} \times e^{-\triangle \epsilon_0/kT*} \times (kT)^{\triangle n} \qquad \ldots (14.27)$$

We may illustrate this with a few simple examples.

(*i*) Consider the dissociation equilibrium, $I_2 \rightleftharpoons 2I$, in which the eqm. constant can be statistically expressed as

$$K_P = \frac{f_I^2}{f_{I_2}} (kT)\, e^{-\triangle E_0/RT} = \frac{f_{I\,(tr)}^2}{(f_{tr} \cdot f_{vib} \cdot f_{rot} \cdot f_{elec})_{I_2}} \times (kT)(e^{-\triangle E_0/RT})$$

$$= \frac{[g_I(2\pi m_I kT)^{3/2}/h^3]^2\, [kT] e^{-\triangle E_0 RT}}{g_{I_2}[(2\pi m_{I_2} kT)^{3/2}/h^3][8\pi^2 IKT/\sigma h^2] e^{-\frac{1}{2}h\nu/kT}\, (1 - e^{-h\nu/kT})^{-1}}$$

$$= \frac{g^2{}_I}{g_{I_2}} \cdot \frac{(\pi m_I kT)^{3/2}}{4\pi^2 Ih} (1 - e^{-h\nu/kT})\, e^{\frac{1}{2}h\nu/kT} \cdot e^{-\triangle E_0/RT}$$

where g_I, g_{I_2} are the statistical weight factors, $\sigma = 2$, $m_{I_2} = 2m_I$ and all the entities are supposed to be in their ground states. The magnitudes of I, ν and $\triangle E_0$ are all determinable from spectroscopic measurements. The equilibrium constant can thus be obtained in terms of spectroscopic constants only.

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In this case, only the translational motion is concerned, hence

$$K_P = \frac{g_{Na^+} \cdot g_\theta}{g_{Na}} \frac{[(2\pi m_+ kT)^{3/2}/h^3]\, [(2\pi m_\theta kT)^{3/2}/h^3]}{[(2\pi m_{Na} kT)^{3/2}/h^3]} \times (kT) e^{-\triangle E_0/RT}$$

$$= \frac{g_{Na^+} \cdot g_\theta}{g_{Na}} \frac{(2\pi m_\theta kT)^{3/2}}{h^3} (kT)\, e^{-\triangle E_0/RT}$$

$$*\phi_0^{\triangle n} = \phi_{0C}^{\,c} \times \phi_{0D}^{\,d} / \phi_{0A}^{\,a} \cdot \phi_{0B}^{\,b} = e^{-[c\epsilon_{0C} + d\epsilon_{0D} - a\epsilon_{0A} - b\epsilon_{0B}]/kT}$$

$$= e^{-\triangle \epsilon_0/kT} = e^{-\triangle E_0/RT}$$

where m_θ = mass of electron, $\triangle E_0$ = the difference of energy of Na-atom and that of Na^+ and electron θ in ground electronic states,

i.e., $\triangle E_0 = V_i . \epsilon$ where V_i is the potential and ϵ, ionisation electronic charge.

(*iii*) In the reaction,
$$\underset{1}{2HI} \rightleftharpoons \underset{2}{H_2} + \underset{3}{I_2}$$

let the three entities of substances be symbolised as 1,2,3 as above.

$$K_P = \frac{f_2 f_3}{f_1^2} e^{-\triangle E_0/RT}$$

Assuming non-degeneracy and also that the entities are in ground electronic state,

$$K_P = \frac{(f_{tr_2} \cdot f_{rot_2} \cdot f_{vib_2})(f_{tr_3} \cdot f_{rot_3} \cdot f_{vib_3})}{(f_{tr_1} \cdot f_{vib_1} \cdot f_{rot_1})^2} e^{-\triangle E_0/RT}$$

$$= \left(\frac{m_2 m_3}{m_1^2}\right)^{3/2} \left(\frac{\sigma_1^2}{\sigma_2 \sigma^3}\right) \left(\frac{I_2 I_3}{I_1^2}\right) \frac{(1-e^{-h\nu_1/kT})^2 \, e^{-\triangle E_0/RT}}{(1-e^{-h\nu_2/kT})(1-e^{-h\nu_3/kT})}$$

The spectroscopic data enables one to calculate the eqm. constant.

14.13. The rate constant of a chemical reaction from thermodynamic principles

The velocities of chemical reactions are profoundly influenced by change in temperature. It was Arrhenius who first showed that the velocity constant (k) of a chemical process increases exponentially with temperature. It was observed that the plot of log k against $1/T$ gives a linear relation. That is,

$$\frac{d \ln k}{dT} = \frac{E}{RT^2}$$

or
$$k = Ae^{-E/RT}$$

where A and E are constants for a given chemical process. A is called the '*frequency factor*' and E, the '*activation energy*' of the reaction.

In a reversible chemical reaction, if k_1 and k_2 be the velocity constants, then

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} \text{ and } \frac{d \ln k_2}{dT} = \frac{E_2}{RT^2}$$

$$\therefore \quad \frac{d \ln k_1/k_2}{dT} = \frac{E_1 - E_2}{RT^2}$$

We have seen, in sec 14.1, that $k_1/k_2 = K$ (eqm. constant).

Hence, $$\frac{d \ln K}{dT} = \frac{E_1 - E_2}{RT^2}$$

But from van't Hoff eqn., $$\frac{d \ln K}{dT} = \frac{\triangle H}{RT^2}$$

Therefore, heat of reaction, $\triangle H = E_1 - E_2$

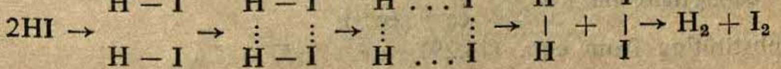
It has now been accepted that molecules must acquire a certain critical energy before they undergo chemical change. In other words, before the chemical reaction the molecules must be raised to a higher energy level and thus be *activated.* The excess or additional energy that the reactant must acquire for chemical change over the average is the energy of activation. The heat of reaction ($\triangle H$) can thus be interpreted as the difference in the energy of activation of the two opposite changes.

Attempts to elucidate the mechanism or the way by which the reactants are converted into products with the help of activation energy led to the proposal of several theories. One of the theories now widely accepted is the '*Transition state theory*' originally proposed by Marcellin and, later on, developed by Eyring and by Polanyi. According to this theory, the reactant molecules are first transformed into an intermediate energy-rich *acivated complex* or *a transition state* from redistribution of energy.

In any case, the activated complex, though unstable and has a transient existence, is treated formally as a definite molecule with an independent entity. The activated complex subsequently breaks up to produce the resultants at a definite rate.

Schematically, Reactants ⇄ Activated Complex → Products

In considering the HI-dissociation, we may visualise it as follows:



$$2HI \rightarrow \begin{matrix} H-I \\ H-I \end{matrix} \rightarrow \begin{matrix} H-I \\ \vdots \quad \vdots \\ H-I \end{matrix} \rightarrow \begin{matrix} H \ldots I \\ \vdots \quad\quad \vdots \\ H \ldots I \end{matrix} \rightarrow \begin{matrix} H \\ | \\ H \end{matrix} + \begin{matrix} I \\ | \\ I \end{matrix} \rightarrow H_2 + I_2$$

As to the activated complex, the following postulates are accepted :

(*a*) The activated complex is regarded as a separate entity, and it is always in equilibrium with the reactant molecules. If C_A and C_B be the concentration of reactants and $C^{\ddagger}$ is the concentration of the activated complex (X) in the reaction,

$$(i)\ \mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X}\ ; \qquad (ii)\ \mathrm{X} \rightarrow \text{Products}$$

the eqm. const., $$K^{\ddagger} = \frac{C^{\ddagger}}{C_A . C_B} \quad \ldots (14.28)$$

or $$C^{\ddagger} = K^{\ddagger} C_A C_B \quad \ldots (14.29)$$

The suffix ($\ddagger$) refers to the activated complex, the concentrations may be expressed as molecules/c.c.

(*b*) The activation energy (*E*) of the reaction is the additional energy which the reactant molecules acquire to form the activated complex (X). The energy of the activated complex will thus be sufficient to reach the peak of the curve in Fig. 14*e*.

(*c*) The activated complex must have one of its vibrational degrees of freedom which would be quite unstable. This vibration is responsible for disrupting the complex into the products. The vibration happens to have a large enough amplitude to break open the complex. The frequency of such vibrations will be low and the average energy will be of the order of kT. If ν be the frequency of this vibration, then

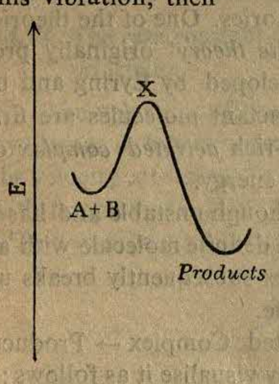


Fig. 14*e*. Variation of energy during transformation

$$h\nu = \epsilon_{vib} = kT, \text{ or } \nu = kT/h,$$

where k = Boltzmann constant and
h = Planck's constant.

Only those of the activated complex molecules which would attain this frequency of vibration per second shall undergo decomposition. In other words, this frequency (ν) would be the rate-determining factor, *i.e.* the rate at which the complex would break up into products.

Hence, rate $= \nu . C^{\ddagger}$, (molecules-$\mathrm{cc}^{-1}\ \mathrm{sec}^{-1}$)

Substituting from eqn. (14.29) rate $= \nu K^{\ddagger} C_A C_B$

If k_1 is the velocity constant of the reaction, then

$$\text{rate} = k_1 C_A C_B$$

Comparing the two, $$k_1 = \nu K^{\ddagger} = \frac{kT}{h} K^{\ddagger} \qquad \ldots (14.30)$$

This will hold true not only for two reactants, but for any reaction.

If the concentrations be taken in moles/litre, the form of this relation would remain the same but the absolute magnitudes of $K^{\ddagger}$ and hence of the rate constant k_1 would only alter. Let the relation then be expressed as

$$k_1' = \frac{kT}{h} K^{\ddagger\prime} \qquad \ldots (14.31)$$

The eqm. constant $K^{\ddagger}$ can be expressed either in terms of thermodynamic quantities or in terms of partition functions. These are taken separately.

(*i*) *From thermodynamic approach* : We know that the eqm. constant of a chemical process, K, is related to the standard free energy change ($\triangle G^\circ$), as,

$$RT \ln K = -\triangle G^\circ \qquad \text{or} \quad K = e^{-\triangle G^\circ/RT}$$

Using Gibbs-Helmholtz relation,

$$K = e^{-\triangle G^\circ/RT} = e^{-(\triangle H^\circ - T\triangle S^\circ)/RT} = e^{\triangle S^\circ/R}.e^{-\triangle H^\circ/RT}$$

Hence, in the formation of the complex here, we can write, for the rate constant, k_1' (eqn. 14.31)

$$k_1' = \frac{kT}{h} K^{\ddagger\prime} = \frac{kT}{h} e^{-\triangle S^{\ddagger}/R}.e^{-\triangle H^{\ddagger}/RT} \qquad \ldots (14.32)$$

when $\triangle S^{\ddagger}$, $\triangle H^{\ddagger}$ are the quantities corresponding to a gm-mole. The superscript zero is dropped for convenience of writing.

Also, $$\ln k_1' = \ln (k/h) + \ln T + \ln K^{\ddagger\prime}$$

i.e., $$\frac{d \ln k_1'}{dT} = \frac{1}{T} + \frac{d \ln K^{\ddagger\prime}}{dT}$$

But from Arrhenius eqn, $\dfrac{d \ln k_1'}{dT} = \dfrac{E}{RT^2}$; (E = energy of activation per mole for complex formation)

$$\therefore \qquad \frac{E}{RT^2} = \frac{1}{T} + \frac{d \ln K^{\ddagger}}{dT}$$

or $E = RT + RT^2 \dfrac{d \ln K^{\ddagger\prime}}{dT} = RT + \triangle U^{\ddagger}$; (van't Hoff isochore)

or $E = RT + \triangle H^{\ddagger} - \triangle nRT$; ($\triangle n$ = change in the no. of moleculcs in complex formation)

or $-\triangle H^{\ddagger} = -E - RT(\triangle n - 1)$

Substituting it in eqn. (14.32),

$$k_1' = \frac{kT}{h} e^{\triangle S^{\ddagger}/R} e^{-E/RT} . e^{-(\triangle n - 1)}$$

i.e., $$k_1' = \left[e^{-(\triangle n-1)} \frac{kT}{h} . e^{\triangle S^{\ddagger}/R} \right] e^{-E/RT} \qquad \ldots (14.33)$$

Comparing with Arrhenius equation ($k_1' = Ae^{-E/RT}$),

the frequency factor, $A = e^{-(\triangle n-1)} . (kT/h) e^{\triangle S^{\ddagger}/R}$ ... (14.34)

In equation (14.33)

for a unimolecular process ($\triangle n = 0$),

$$k_1' = e.(kT/h) e^{\triangle S^{\ddagger}/R} e^{-E/RT}$$

for a bimolecular process ($\triangle n = -1$),

$$k_1' = e^2 (kT/h) e^{\triangle S^{\ddagger}/R} e^{-E/RT}, \text{ etc.}$$

For gaseous reactions, the entropy of activation ($S^{\ddagger}$) is generally negative and varies little with temperature. Its magnitude varies between -10 cal ~ -40 cal/mole-°K. Since $k/h = 2 \times 10^{10}$, the velocity constant for a bimolecular reaction will have values between

$$k_1 \approx 2 \times 10^{10} T e^{-5} e^{-E/RT} \text{ and } k_1 \approx 2 \times 10^{10} T e^{-20} e^{-E/RT}$$

Problem. 15. For the unimolecular process of conversion of cyclopropane into propylene, the energy of activation is $E = 65000$ cal at 500°C. Estimate the entropy of activation.

Given $\log k_1 = 15.17 - \dfrac{65000}{2.3RT}$

The rate constant, $k_1 = e \dfrac{RT}{Nh} e^{\triangle S^{\ddagger}/R} e^{-E/RT}$

Using standard values, $k_1 = 4.4 \times 10^{13} \, e^{\triangle S^{\ddagger}/R} . \, e^{-65000/2 \times 773}$

Since $\log k_1 = 15.17 - 65000/(2.3RT)$, $k_1 = 1.48 \times 10^{15} e^{-65000/(2 \cdot 3RT)}$

Equating the frequency factor, $4.4 \times 10^{13} \, e^{\triangle S^{\ddagger}/R} = 1.48 \times 10^{15}$

whence, $\triangle S^{\ddagger} = 7$ cal/mole-degree.

(ii) From Partition functions : The eqm. constant for a reaction, say, A + B $\rightleftharpoons$ C, can be expressed with the help of partition function, as

$$K = \frac{f_C}{f_A f_B} e^{-E_0/RT} ; \quad \text{(equation 14.27).}$$

So, in the formation of the activated complex (X), the eqm. constant would be,

$$K^{\ddagger} = \frac{f_X^{\ddagger}}{f_A f_B} e^{-E_0/RT}$$

where E_0 = energy increase at absolute zero when one mole of activated complex is formed and $f_X^{\ddagger}$ = total partition function of the complex.

The total number of degrees of freedom for a molecule of N-atoms is $3N$, of which three are rotational and three translational. Therefore, the vibrational degrees of freedom would be $3N-6$. Out of the vibrational degrees of freedom of the activated complex, one is different for which the frequency is quite low to allow the breaking up of the complex into products. Hence, partition function for the vibrational degrees of freedom may be written as $f_X^{\ddagger}.f_v'$, where $f_X^{\ddagger}$ denotes the partition function for all degrees of freedom excepting the vibrational component of the critical mode and f_v' for the vibration for which the frequency $\nu \rightarrow 0$.

Hence $$K^{\ddagger} = \frac{f_X^{\ddagger}.f_v'}{f_A f_B} e^{\frac{-E_0}{RT}} \quad \ldots \text{(A)}$$

For the degree of freedom of a vibration (eqn. 11.52),

$$f_v' = (1-e^{-h\nu/kT})^{-1}$$

So, $$f'_{v(\text{Lim } \nu\rightarrow 0)} = \frac{1}{1-e^{-h\nu/kT}} = \frac{1}{1-(1-\frac{h\nu}{kT})} = \frac{kT}{h\nu}$$

Substituting this in (A) ; $K^{\ddagger} = \frac{kT}{h\nu}.\frac{f_X^{\ddagger}}{f_A f_B} e^{-E_0/RT}$

But the reaction rate = $\nu C^{\ddagger} = \nu K^{\ddagger}.C_A C_B$

But the rate is = $k_1 C_A C_B$; (k_1 = rate constant).

$$\therefore \quad k_1 = \nu K^{\ddagger} = \frac{kT}{h}.\frac{f_X^{\ddagger}}{f_A.f_B} e^{-E_0/RT} \quad \ldots (14.35)$$

Comparing with Arrhenius Equation, $k_1 = Ae^{-E_0/RT}$,

$$A = \frac{kT}{h} \cdot \frac{f_X^{\ddagger}}{f_A f_B} \qquad \ldots (14.36)$$

If two molecules containing n_A and n_B atoms form a complex (X), then the partition functions would be

$$f_X^{\ddagger} = f_t^3 f_r^3 f_v^{3(n_A+n_B)-7} \; ; f_A = f_t^3 f_r^3 f_v^{3n_A-6} \; ; f_B = f_t^3 f_r^3 f_v^{3n_B-6}$$

where f_t, f_r and f_v are the contributions to translational, rotational and vibrational degrees of freedom.

$$\text{Hence} \quad k_1 = \frac{kT}{h} \cdot \frac{f_X^{\ddagger}}{f_A f_B} e^{-E_0/RT}$$

$$= \frac{kT}{h} \cdot \frac{f_t^3 f_r^3 f_v^{3(n_A+n_B)-7}}{f_t^3 f_r^3 f_v^{3n_A-6} \times f_t^3 f_r^3 f_v^{3n_B-6}} e^{-E_0/RT}$$

$$= \frac{kT}{h} \left(\frac{f_v^5}{f_t^3 f_r^3} \right) e^{-E_0/RT}$$

At ordinary temperatures, $kT/h \approx 10^{13}$, and $f_v \approx 1$, $f_r \approx 10$, $f_t \approx 10^8$, hence

$$k_1 = 10^{13} \times \frac{1}{(10^8)^3 \times 10^3} = 10^{-14} \text{ cc molecules}^{-1} \text{ sec}^{-1}$$

$$\approx 10^7 \text{ litre moles}^{-1} \text{ sec}^{-1}$$

This approximately corresponds to the experimental results.

Problems

1. At 100°C, the vapour density of nitrogen tetroxide is 25 at 1 atm. Show that $K_p = 9.6$.

2. If α be the degree of dissociation of NH_3 at pressure P, prove that $\alpha = [1 + 1.33\, P/K_p]^{-\frac{1}{2}}$

3. Prove that the maximum conc. of ammonia in its synthesis can be obtained only when $N_2 : H_2$ is in the molar ratio 1 : 3.

4. N_2 and O_2 combine at a given temperature to produce NO. At eqm. the yield of NO is x per cent by volume. If

$$x = \sqrt{Kab} - \frac{K(a+b)}{4}$$

where K is the eqm. constant at the given temperature and 'a' and 'b' are the volume percentages of N_2 and O_2 respectively in the initial pure mixture, what should be the initial composition of the reaction mixture in order that maximum yield of NO is ensured? (C.U.'74). **Ans.** $N_2 = 50\%$

5. A mixture of SO_2 and O_2 in molar ratio (2 : 1) was kept over a Pt-catalyst in a reaction vessel at 650°C, the total pressure was 10 atm. If 60% SO_2 be converted into SO_3 in this process, calculate K_p for the reaction,

$$2SO_2+O_2 = 2SO_3$$

State, with reasons, whether the above eqm will be disturbed and if so in which direction, when

(*i*) volume of reaction vessel is increased at constant temp.

(*ii*) N_2 is introduced into the vessel to increase total pressure at constant temp. and volume.

(*iii*) the catalyst is removed at constant temp. and volume without disturbing the gas.

(*iv*) the reaction vessel is suddenly cooled to 0°C. [C.U. 1973]

6.(*a*) At a total pressure of 0.5 atm, PCl_5-vapour has a density of 89 ($H = 1$). What is the partial pressure of chlorine when the vapour is compressed to one atmosphere isothermally?

(*b*) If an equal volume of chlorine at the same temp. and pressure be introduced into the mixture at 0.5 atmosphere isothermally, what will be the partial pressure of PCl_3? **Ans.** (*a*) 0.11 atm. (*b*) 0.012 atm.

7. What will be the pressure of CO_2 at eqm. in the reaction, $CaCO_3 \rightleftharpoons CaO + CO_2$, at 25°C if standard molal thermodynamic potentials are,

$$\mu^{\circ CaCO_3} = -270 \text{ Kcal}, \quad \mu^{\circ CaO} = -144.5 \text{ Kcal} \quad \mu^{\circ CO_2} = -94.4 \text{Kcal}.$$

Ans. $p_{CO_2} = 1.6\times10^{-23}$ atm.

8. In the dissociation of Iodine vapour,

$$I_2(g) \rightleftharpoons 2I(g), \ \Delta H = 120950 \text{ j/mole}.$$

Show that at ordinary temperatures (27°C), the eqm-constant K increases nearly five times for every ten degree rise in temperature.

9. The standard enthalpy and free-energy of formation of nitric oxide are

$$\Delta H_f{}^{\circ} = 21600 \text{ cal}, \ \Delta G_f{}^{\circ} = 20720 \text{ cal}$$

Calculate K_p for the reaction, $N_2+O_2 \rightleftharpoons 2NO$ at 2000°K. **Ans.** 3.8×10^{-4}

10. At 0°C and at 27°C, the concentrations of H^+ ions in pure water are 0.4×10^{-7} and 1.2×10^{-7} respectively. Find out the heat of ionisation of water.

11. At 2000°K, ΔG for the reaction, $N_2+O_2 \rightleftharpoons 2NO$, is given by $\Delta G^{\circ} = 22000-2.5\ T$. Estimate K_p at 2000°K. **Ans.** 1.4×10^{-2}

12. In the gaseous reaction : $S_2+2O_2 = 2SO_2$ (25°C) $\Delta H^{\circ} = -173$ Kcal, $\Delta S^{\circ} = -33.6$ eu, $\Delta C_p{}^{\circ} = -1.49 + 1.42\times10^{-3}T$. Find the value of K_p at 1000°C.

13. The following heats of formation and absolute entropies are given :

	H_2	H_2O	CO	CO_2
$\Delta H_f{}^{\circ}$ (cal)	—	−57800	−26420	−94094
S° (eu)	31.2	45.1	47.3	51.0

Calculate K_p for the reaction, $CO+H_2O \rightleftharpoons CO_2+H_2$ at 500°K assuming $\Delta H_f°$-values are independent of temperature.

14. For the reaction, $CuSO_4, 3H_2O \rightleftharpoons CuSO_4, H_2O + 2H_2O\ (g)$, the dissociation pressure is 7×10^{-3} atm at 25°C and $\Delta H° = 27000$ cal. What will be the dissociation pressure at 127°C?

15. In the gaseous reaction, $2A+B \rightleftharpoons A_2B$, $\Delta G° = -1200$ cal at 227°C. What total pressure would be necessary to produce 60% conversion of B into A_2B when 2 : 1 mixture is used?

16. Calculate $\Delta H°$, $\Delta G°$, $\Delta S°$ for the reaction, $NiO\ (s)+CO \rightleftharpoons CO_2+Ni\ (s)$ at 1000°K. Given

$$K_{P_{(950°K)}} = 4.6\times10^3,\ K_{P_{(1025°K)}} = 2.5\times10^3,\ K_{P_{(1125°K)}} = 1.6\times10^3$$

Ans. $\Delta H° = -47450$ cal

17. At 1 atm, the percentage decomposition of carbon dioxide are 2×10^{-5} and 1.3×10^{-2} at 727°C and 1127°C respectively, according to the reaction,

$$2CO_2 = 2CO+O_2$$

Calculate $\Delta G°$ and $\Delta S°$ for the reaction at 1000°C assuming ΔH as constant.

Ans. $\Delta G_{1000} = -93370$ cal

18. In the isolopic exchange reaction, $H_2 + D_2 = 2HD$, (the entities are indicated by 1, 2 and 3), the following spectroscopic data are known,

	H_2	D_2	HD
$\nu\times10^{-12}s^{-1}$	132.3	93.7	114.8
$I\times10^{41}$ g-cm^2	4.6	9.19	6.13

The heat of disociation of the three isotopes may reasonably be taken to be equal, $D_{H_2} = D_{D_2} = D_{HD}$

and $\sigma_{H_2} = \sigma_{D_2} = 2$; $\sigma_{HD} = 1$

Show that (*i*) $\Delta E_0 \approx 172$ cal/mole

$$\text{and} \quad K = \left[\frac{M_3^2}{M_1M_2}\right]^{3/2} \cdot \frac{\sigma_1\sigma_2}{\sigma_3} \cdot \frac{I_3^2}{I_1I_2} e^{-\Delta E_0/kT}$$

Calculate the value of K at 25°C. Ans. 3.27

CHAPTER 15

HETEROGENEOUS EQUILIBRIA : THE PHASE RULE

15.1. The Heterogeneous Systems

When a system consists of parts which have different physical properties (perhaps also different chemical properties) and which are separated by bounding surfaces, the system is said to be a heterogeneous one. When the chemical or physical reactions which occur involve a movement from one state to another state of aggregation, *i.e.*, from one phase to another, the equilibrium attained is spoken of as heterogeneous. Such equilibria therefore occur in vaporisation, condensation, dissolution, precipitation, transition of one form into another ($S_\alpha \rightarrow S_\beta$), distribution of solids between two immiscible solvents, chemical changes having reactants and resultants in different states of aggregation etc. The study of equilibria in heterogeneous systems is always based on some basic thermodynamic principles.

When information regarding the quantitative relation between the reacting species is required, the application of the mass action Law is inescapable whether the system is homogeneous or heterogeneous.

In a heterogeneous system, the constitueunts would occur in more than one state or phase, say liquid and vapour. A change in temperature would lead to a change of pressures or concentrations. These changes would be governed by Clapeyron equation and the Raoult's Law,

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \text{and} \quad p_i = xP.$$

The chemical potential of a component in different phases at equilibrium is the same and hence Nernst distribution Law (Sec 10-11*a*) provides information regarding the concentrations of the components in different phases. Besides these, the most important principle used universally for the study of heterogeneous equilibria is the 'Phase Rule'.

The phase rule put forward by Willard Gibbs (1876) from precise thermodynamic considerations, is the most useful generalisation concerning the equilibria in heterogeneous systems. The phase rule is a relation between the number of components (C), the number of phases (P) and the variable parameters (F) called degrees of freedom of a heterogeneous system at equilibrium. The relation is expressed as,

$$F = C - P + 2$$

The beauty of the phase rule lies in its extraordinary simplicity and the capacity of bringing within its ambit most widely divergent and unrelated heterogeneous equilibria. Before we proceed to derive this principle, it would be necessary to define the terms involved, namely phases, components and the degrees of freedom.

Phases. *A phase is defined as a physically distinct but homogeneous part of a system separated from other parts by boundary surfaces.* A heterogeneous system is therefore composed of two or more phases. Thus a system containing water and its vapour has two phases—the liquid phase and the vapour phase ; each phase is homogeneous and distinct and there is the surface-boundary between the two. A gas mixture is always a single phase. Similarly, all homogeneous solutions are one-phase systems, whatever may be the number of substances present in the same. Every solid, however, constitutes a separate phase. So, when calcium carbonate dissociates into calcium oxide and carbon dioxide, there are two solid phases—viz. calcium carbonate and calcium oxide—and one gas phase of carbon-dioxide. That is, it is a three-phase heterogeneous system.

Components. In dealing with the heterogeneous systems, it is necessary to define another term, the components of a system. *The minimum number of independent chemical constituents by which the composition of every phase of the system can be expressed determines the number of components.* It must be clearly understood that the components of a system are not synonymous with the consituents of the system. All the constituents need not be components but all the components must be included in the constituents.

To illustrate : The system water-water vapour contains only one component. Both the phases may be expressed by one chemical individual namely, H_2O. It is a one-component system. A cane-sugar solution will be a two-component system as there are two independent chemical substances which determine the composition of the solution, namely, H_2O and $C_{12}H_{22}O_{11}$ (cane sugar). Again, ferric chloride and water can give rise to solids like $Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$, $Fe_2Cl_6.4H_2O$ and anhydrous Fe_2Cl_6, as also the solution, ice and the vapour phase. But to express the composition of any phase, two chemical individuals—H_2O and Fe_2Cl_6—are only required. It is thus a two-component system.

If a system contains calcium carbonate at a higher temperature, three substances are likely to be present in the system viz, calcium carbonate, calcium oxide and carbon dioxide.

$$CaCO_3 = CaO + CO_2$$

There is however a restriction that the amount of CaO and CO_2 must be equivalent. As such, the composition of any phase can be represented by the concentrations of any two of the three individuals ; say, CaO and CO_2. The phase calcium carbonate is lCaO + $l$$CO_2$; the phase calcium oxide is mCaO + $0CO_2$; and the gas phase carbon dioxide is mCO_2 + 0CaO. Hence, although three constituents occur in the system, it is really a two-component system.

As a general rule, the number of components (C) is obtained by subtracting the number of restrictions (q) imposed from the total number of individual constituents (C') present in the system; *i.e.*, $C = C' - q$. In the case cited above, there are three constituents and one restriction (equivalence of CaO and CO_2), hence the number of components,

$$C = 3-1 = 2$$

Likewise in a dilute solution of sugar, there is no restriction and there are two constituents, therefore number of components,

$$C = 2-0 = 2$$

Degrees of freedom : We shall now consider the general thermodynamic criteria which would govern the equilibria between the different phases of a heterogeneous system. Suppose we are to enquire about the conditions which would keep a liquid in equilibrium with its vapour. It is a well-known observation that if we simply fix the temperature or the pressure, the desired equilibrium will be maintained. This fact may also be thermodynamically arrived at, not only for this system but for any multiphase system which may contain a large number of components. The thermodynamic parameters used to define a heterogeneous system are the usual pressure, temperature and volume (or concentration); other conditions such as gravitational field, magnetic field, etc. are not taken into account. In this connection, it would be convenient to introduce a new term, namely the *degrees of freedom.*

If the state of a system cannot be completely defined until at least F data are given, we say that the system has F degrees of freedom. It means that the state of the system depends on F independent variables. *The number of degrees of freedom may then be defined as the number of variables that must be specified in order to define the system completely*. We can also indicate another definition for the number of degrees of freedom. *The number of degrees of freedom of a system is the number of factors (temperature, pressure, concentrations, etc.) which can be varied independently without altering the number of phases*. This may be explained with an illustration.

Suppose a gas is enclosed in a cylinder with a movable piston as in Fig. 15*a*(I). It is a one-phase system. Let the volume of the gas be intentionally kept constant, we can now alter the temperature and pressure without altering the number of phases. Instead, when the temperature be fixed, the other two factors pressure and volume can be varied and therefore the state of the system remains undefined. But if we fix two of the factors—say, temperature and pressure—then the third (volume) is definite. So, by fixing two variable factors, the system is completely defined. Such a system in which two factors can be independently varied without changing the number of phases has two degrees of freedom or it is a bi-variant system.

Again, suppose a liquid is in contact with its vapour as in Fig. 15*a*(II). In this case if we fix either the temperature or the pressure, the system is defined completely, subject to the condition of the co-existence of both the phases. For any given temperature, the vapour pressure is immediately fixed. If at a fixed temperature, pressure is altered, one of the phases would disappear. So, this is a system with one independent variable factor or it is a univariant system possessing one degree of freedom.

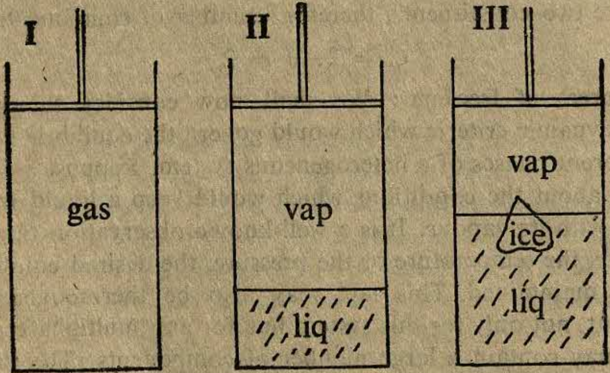


Fig. 15*a*

Further, suppose the system in Fig. 15*a* (III) contains a substance in equilibrium in three phases—say, ice, liquid water and water vapour. This is possible at a particular pressure and temperature. If we vary any one of these factors, either pressure or temperature, one of the phases would disappear. If we lower the temperature, all liquid will solidify and if we raise the temperature the ice will disappear. Hence in this case there is no independent variable or it is a non-variant system, the number of degrees of freedom being zero.

From the thermodynamic standpoint, it would be interesting to find out the independently variable factors or conditions for a number of components existing in equilibrium in different phases. The answer is provided by the Phase Rule.

15.2. The phase rule

The phase rule expresses the condition of equilibrium by the relation between the number of the co-existing phases and the components. Consider a heterogeneous system of P number of phases (denoted by superscripts $a, b, \ldots p$) containing C number of components (denoted by subscripts, 1, 2, 3, . . .c) in equilibrium. The concentrations of any component in the different phases may be different. The system is a closed one and it is in mechanical and thermal equilibrium, meaning that all the phases are at the same temperature T and under the same pressure P. It may be assumed that there is no chemical reaction between the substances in the system.

The chemical potentials (μ) of the different components in the P-phases are represented as

$$\mu_1^{(a)}, \mu_2^{(a)}, \ \ldots \ \mu_C^{(a)}; \qquad \mu_1^{(b)}, \mu_2^{(b)}, \ \ldots \ \mu_C^{(b)};$$

$$\mu_1^{(c)}, \mu_2^{(c)}, \ \ldots \ \mu_C^{(c)}; \ \ldots \qquad \mu_1^{(p)}, \mu_2^{(p)}, \ \ldots \ \mu_C^{(p)}.$$

Now, imagine small amounts (dn moles) of the components are transferred, under equilibrium conditions, from one phase to another. The following conditions would then hold true.

$$\begin{aligned} dn_1^{(a)} + dn_1^{(b)} + dn_1^{(c)} + \ldots dn_1^{(p)} &= 0 \\ dn_2^{(a)} + dn_2^{(b)} + dn_2^{(c)} + \ldots dn_2^{(p)} &= 0 \\ \ldots \qquad \ldots \qquad \ldots \quad & \\ dn_C^{(a)} + dn_C^{(b)} + \qquad \ldots \ dn_C^{(p)} &= 0 \end{aligned} \qquad \ldots (15.1)$$

Further, from Gibbs-Duhem relation, at equilibrium we have,

$$dG = \Sigma \mu dn = 0.$$

Hence,

$$\begin{aligned} &\mu_1^{(a)}\, dn_1^{(a)} + \mu_1^{(b)}\, dn_1^{(b)} + \ldots + \mu_1^{(p)}\, dn_1^{(p)} \\ &+ \mu_2^{(a)}\, dn_2^{(a)} + \mu_2^{(b)}\, dn_2^{(b)} + \ldots + \mu_2^{(p)}\, dn_2^{(p)} \\ &+ \qquad \ldots \qquad \ldots \\ &+ \mu_C^{(a)}\, dn_C^{(a)} + \mu_C^{(b)} dn_C^{(b)} + \ldots + \mu_C^{(p)} dn_C^{(p)} = 0 \end{aligned} \qquad \ldots (15.2)$$

Multiplying equations (15.1) by c-different multipliers (λ) we find,

$$\begin{aligned} \lambda_1 dn_1^{(a)} + \lambda_1 dn_2^{(b)} + \dots + \lambda_1 dn_1^{(p)} &= 0 \\ \lambda_2 dn_2^{(a)} + \lambda_2 dn_2^{(b)} + \dots + \lambda_2 dn_2^{(p)} &= 0 \\ \dots \qquad \dots \qquad & \qquad \dots (15.3) \\ \lambda_C dn_C^{(a)} + \lambda_C dn_C^{(b)} + \dots + \lambda_C dn_C^{(p)} &= 0 \end{aligned}$$

Adding the equations (15.2) and (15.3) we can pick up and equate the coefficients of each of the *dn*-terms to zero. The results would be,

$$\begin{aligned} -\lambda_1 &= \mu_1^{(a)}, \quad -\lambda_1 = \mu_1^{(b)}, \quad \dots -\lambda_1 = \mu_1^{(p)} \\ -\lambda_2 &= \mu_2^{(a)}, \quad -\lambda_2 = \mu_2^{(b)}, \quad \dots -\lambda_2 = \mu_2^{(p)} \\ \dots & \qquad \dots \qquad \dots \\ -\lambda_C &= \mu_C^{(a)}, \quad -\lambda_C = \mu_C^{(b)}, \quad \dots -\lambda_C = \mu_C^{(p)} \end{aligned}$$

That is,

$$\begin{aligned} \mu_1^{(a)} &= \mu_1^{(b)} = \dots = \mu_1^{(p)} \\ \mu_2^{(a)} &= \mu_2^{(b)} = \dots = \mu_2^{(p)} \\ \dots & \qquad \dots \qquad \qquad \dots (15.4) \\ \mu_C^{(a)} &= \mu_C^{(b)} = \dots = \mu_C^{(p)} \end{aligned}$$

These are the equations of the phase equilibrium. Thus, we know from the thermodynamic considerations that at equilibrium the chemical potentials of a constituent in all the phases of the system must be the same. Different constituents, of course, have different chemical potentials.

Now, let us first determine the total number of variable factors in the given system. So far as the composition variables are concerned, in every phase we may have C components having C different concentrations. But in a closed system, if we arbitrarily choose concentrations of $(C-1)$ components, the last one is fixed by the remainder. So, there are really $(C-1)$ composition variables in each phase. For all the P-phases, the number of composition variables would be $P(C-1)$. In addition, there are two other variables, namely, temperature and pressure.

Hence the total number of variables $= P(C-1)+2$ ...(15.5)

Next let us see how many of these variables are already fixed and cannot be altered. From equations (15.4) it is known that if the chemical potential of a component in any of the P-phases be defined, its chemical potentials in the other $(P-1)$ phases cannot be varied. The chemical potentials are related to the concentrations. As such if the concentration of a component in any one phase be arbitrarily fixed, then the concentrations of the same component in the other $(P-1)$ phases would be fixed, *i.e.*, non-variant. For this particular component, $(P-1)$ composition variables are fixed. For all the C-components, the number of composition variables thus immobilised would be $C(P-1)$. If we subtract this number from the total number of possible variables of the system we shall get the number of variables of the system which can be arbitrarily chosen. This would represent the number of the degrees of freedom (F) of the system.

$$F = P(C-1) + 2 - C(P-1)$$

or

$$F = C-P+2 \qquad \ldots (15.6)$$

This is the 'Phase Rule'.

The systems are named univariant, bivariant, trivariant, etc. according as the degrees of freedom are 1, 2, 3, etc. The Phase Rule takes into account only the variables of temperature, pressure and the composition and the influence of other factors such as electric, magnetic, gravitational, surface forces, etc. is ignored. The equation does not depend upon the nature or the amount of the substances. It also does not assume anything regarding the constitution of the matter or the molecular complexity. The Phase Rule tells us that the systems having the same degrees of freedom shall behave in a similar fashion. It thus enables us to classify the states of equilibrium. It is immaterial whether the phase-changes in systems are chemical or physical, if the number of degrees of freedom be the same, the systems shall behave similarly when temperature, pressure and composition (concentrations) are varied.

To illustrate : We may take the following three different systems, namely, (*i*) Water and its vapour (*ii*) Solid β-tin and its vapour and (*iii*) Solid calcium carbonate in contact with its dissociated products calcium oxide and carbon dioxide. The last system involves a chemical reaction while the other two are physical changes. The details of the systems are :

System	Co-existing phases	Number of phases and components	Degrees of freedom
Water and vapour	liquid-gas	$P = 2, C = 1$	$F = 1-2+2 = 1$
Tin and its vapour	solid-gas	$P = 2, C = 1$	$F = 1-2+2 = 1$
Calcium carbonate	solids-gas	$P = 3, C = 2$	$F = 2-3+2 = 1$

We have already seen previously that the number of components in the system in which calcium carbonate is dissociated is two.

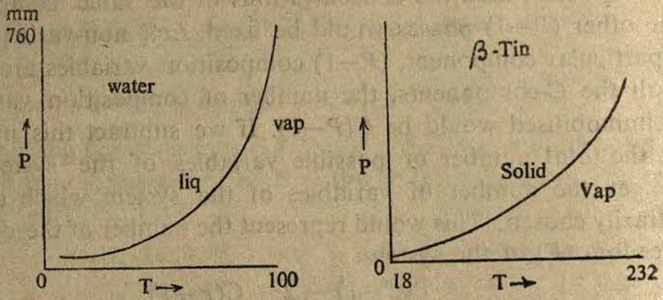
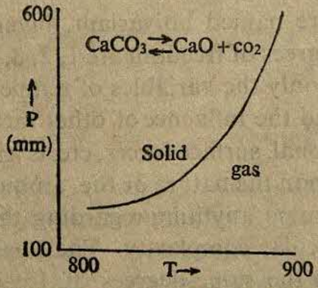


Fig. 15*b*. (*i*) Water and its vapour (*ii*) Tin and vapour



(*iii*) Dissociation of $CaCO_3$

Now all the systems, in accordance with the Phase Rule, are univariant and hence all of them are expected to behave similarly. The experimentally observed variation of vapour pressures with temperature for the three systems are given in Figs. 15*b*.

The similarity of the curves indicates that although the system are widely different yet they behave in like manner. Alternatively, from a knowledge of the degrees of freedom and the number of components present it is possible to predict the number of phases coexisting in the system under equilibrium. Such a study would therefore enable us to state whether a given system is a homogeneous or a heterogeneous mixture. With the help of the phase rule we have grouped together widely different phenomena and it guides us to ascertain the existence of a new phase. The law of mass action cannot provide us with such information. When A and B reacts, the law of mass action would give quantitative relations of the equilibrium concentrations but the law cannot predict if any compound A_xB_y has been formed as a new phase or not. The phase rule has been of great value in the practical field such as in the isolation of salts from mixtures, preparation of alloys, etc. It helps in the adjustment of temperature, composition etc. to obtain a desired product. The preparation of potassium chloride from Stassfurt deposits in an outstanding example.

15.3. The Phase Rule for systems with reactive components

In deducing the phase rule equation (15.6), it was tacitly assumed that the components do not undergo any chemical change between them. But if some components undergo chemical changes, the equation has to be modified. The composition variables are governed by the equality of chemical potentials of a component in different phases at equilibrium. Now if there is a chemical reaction, then apart from the fixed composition variable indicated above, the stoichiometric conditions would also come into play. For a given concentration of a component involved in a chemical change in the system, the concentrations of other components participating in the same will become fixed. This amounts to the imposition of some additional restrictions on the composition variable. The number of such restrictions depend upon the number of reactants and resultants involved. If Q denotes such restrictions, the number of degrees of freedom would be diminished by Q. In such a case, the degree of freedom will be given by,

$$F = [C'-P+2]-Q, \qquad \ldots (15.7)$$

where C' is the total number of constituents in the system.

In other words, the phase rule equation would be

$$F = C-P+2\ , \quad \text{where } C = C'-Q \qquad \ldots (15.8)$$

That is, the number of components in the equation should be reduced by the number of restrictions.

Besides the chemical reactions, there may arise other conditions which would restrict the number of free variables. For example, if a one-component system be at the critical point, the the liquid and vapour phases are identical. In this case, the number of degrees of freedom would be

$$\begin{aligned} F &= C-P+2-Q \\ &= 1-2+2-1 = 0 \end{aligned}$$

i.e., the critical state would be an invariant point.

15.4. Phase Diagrams

The effect of changes in temperature, pressure or composition on the changes of phase in a system can be easily understood only when these are graphically represented. The conditions under which the different phases can co-exist are conveniently described by graphs called *phase diagrams*. That is why phase diagrams are universally employed in the application of phase rule to heterogeneous systems. When there are only two variables, such as pressure and temperature, or temperature and concentration, rectangular coordinates are used. But when three variables are concerned, solid diagrams are needed. Time is not a variable since phase diagrams are concerned with systems in equilibria. The total quantities of the components are also not of any importance but their concentrations are. A number of phase diagrams of different types will be illustrated in the pages following. But a few elementary facts may be mentioned here.

The effect of pressure on the temperature of transition from one phase to another of a substsnce is governed by the Clapeyron equation.

$$\frac{dp}{dT} = \frac{\triangle H}{T\triangle V} = \frac{\triangle S}{\triangle V} \qquad \ldots (15.9)$$

The plot of P vs T would reveal the conditions of equilibrium between two phases, say, liquid-vapour, solid-liquid etc. (Fig. 15*c*). We may consider the general behaviour of such transformations.

(*i*) In the transformation from liquid → vapour, both $\triangle S$ and $\triangle V$ are positive. Hence dp/dT is also positive as in OA (Fig. 15*c*).

The molar entropy-change $\triangle S$ in the vaporisation of a liquid is of the order 10 e.u. and volume change approximately 10^4 c.c./mole. Hence, $dp/dT = 10/10^4$ $\approx 10^{-3}$ cal cc^{-1} degree^{-1} $\approx$ 0.04 atm/degree.

(*ii*) In the transformation solid → vapour, again $\triangle S$ and $\triangle V$ are both positive. Hence the slope $\frac{dp}{dT}$ is positive as in OB.

The volume-change $\triangle V$ is almost the same as in (*i*), but $\triangle S$ is much larger, so that dp/dT will be a steeper slope than in the transformation liquid → vapour.

In the neighbourhood of the triple-point, the P-T curve OB for solid/vapour will ascend more rapidly than that for the liquid/vapour (OA). The two curves (OA) and (OB) are not continuous and must intersect.

(*iii*) In the transformation solid → liquid, $\triangle S$ is positive but $\triangle V$ may have a positive or a negative value. Hence, the slope dp/dT may be positive or negative.

The molar entropy change $\triangle S$, in fusion is of the order of 5 e.u. and the molar $\triangle v = 5$ c.c. So,

$$\frac{dp}{dT} = \pm \frac{\triangle s}{\triangle v} \approx \pm 1 \text{ cal cc}^{-1} \text{ degree}^{-1} \approx \pm 40 \text{ atm/degree}$$

$$\text{or} \quad \frac{dT}{dP} \approx \pm 0.02 \text{ degree/atmosphere}$$

Hence, the slope of P-T curve for solid/liquid transformation (OC) will be very steep. One atmosphere change in pressure would change the fusion temperature by 0.02°C only.

The line OC in the figure is the locus of points (P, T) at which the solid and liquid (s/l) can co-exist. Similarly the other curves I and II indicate the locus of points for co-existence of other phases, l/g and s/g. Points on the right of a line indicates one phase and points on the left another phase. Areas bounded by the lines indicate the existence of a single homogeneous phase.

The point of intersection of any two curves will indicate co-existence of all the three phases solid-liquid-vapour in eqm. The point is called a *triple* point.

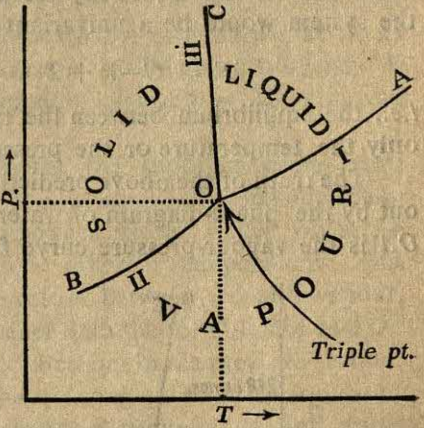


Fig. 15*c*

The triple point temperature of some systems are given :

System :	H_2O	NH_3	HCl	CH_4	I_2
T_{tr} °K :	273.01	195.3	159.3	90.6	386.7

We can now consider some simple systems. Phase diagrams are classified on the basis of number of components such as one-component system, two-component system, etc.

ONE COMPONENT SYSTEMS

15.5. The System, H_2O

One component systems shall comprise of a pure substance only. The simplest and a typical example will be that of a system containing water. Under ordinary circumstances there are three possible phases, ice, water and water vapour.

(*a*) If the system consists of only one phase, say vapour, then

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

the system would be bivariant according to the Phase Rule. That is, both pressure and temperature can be varied simultaneously without any change in its phase or both the pressure and temperature variables must be determined to define the state of the system.

(*b*) If the system contains two phases in equilibrium, say, water and its vapour, or say ice and water, or ice and vapour, the system would be a univariant one. For

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

i.e., the equilibrium between the two phases would be known if only the temperature or the pressure be fixed.

The truth of the above predictions of the Phase Rule is borne out by the phase-diagram of water as given in Fig 15*d*. The line *OA* is the vapour-pressure curve for water, the vapour pressure

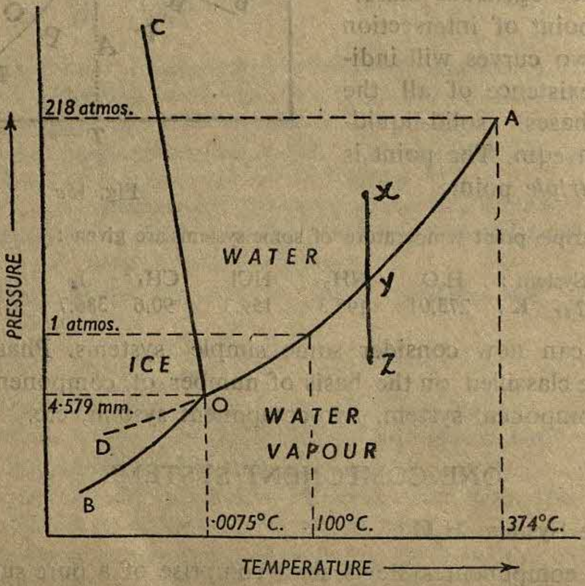


Fig. 15*d*. The phase-diagram for water (not to scale)

increasing with rise in temperature. The points on this line show the pressure of water vapour under which water and its vapour exist in equilibrium at different temperatures. This curve *OA* then represents the univariant states of the system water/vapour. For any given temperature, equilibrium vapour pressure is fixed, *i*.e, there is one variable only. For any point *x* above *OA*, the system would be liquid water. If the pressure is lowered at constant temperature, the vapour phase would appear at the point *y*.
On further lowering of pressure, to *z*, the system would be completely vapour (temp. remaining constant). Hence *OA* in the phase diagram is the demarcation or boundary line between two phases, water and its vapour.

There is however an upper limit for *OA* terminating at *A*, its critical state, when the liquid phase is no longer distinguishable from vapour phase. The coordinates of *A* are $p = 218$ atm and $t = 374°\text{C}$.

Similarly the curve *OB* denotes the vapour-pressure curve of ice or more appropriately the sublimation pressure-temp. curve for ice. It registers the vapour-pressures under which ice is in equilibrium with its vapour at different temperatures. This curve is also the line of demarcation between ice and vapour. The slope of *OB* is however steeper than that of *OA*; *OA* and *OB* are not continuous as has been pointed out in the previous section.

On the other hand, *OC* is the freezing point curve indicating the equilibria at different temperatures between ice and water. The line has a negative slope, *i.e.*, melting point is lowered with increase in pressure, the density of solid ice being less than that of water.

Each of the three lines *OA*, *OB* and *OC* indicates the two-phase equilibria and represents univariant states. The areas enclosed between these lines represent regions of a single phase *i.e.*, bivariant states of the system. Thus the region *AOB* is vapour, *BOC* ice and *COA* water.

The point *O*, where the three lines meet, all the three phases, ice, water and vapour should co-exist. This is called a *triple point*. The pressure at this point has been found to be 4.58 mm. The freezing point of water is 0°C under 760 mm pressure, and from Clapeyron equation, the freezing point changes by 1° when pressure is changed by about 140 atmospheres. Hence at 4.58 mm the freezing point will be raised to + .0075°. That is, the triple point has $p = 4.58$ mm, $t = 0.0075$°C.*

Since there are three phases ; $F = 1-3+2 = 0$ *i.e.*, the system is non-variant at the triple point. If either the temperature or the pressure is changed, the three phases would not co-exist, one of the phases would disappear.

It is however possible to cool water below its freezing point without solidification. The liquid below its freezing point is said to remain in *supercooled state*. This supercooled state is not quite stable and it is usually described as a *metastable state*. The supercooled water has also its vapour pressure which changes with temperature. The vapour pressure curve of supercooled water is given by OD (the dotted line in the figure) which is a continuation of AO. The line OD is above OB, the vapour pressure curve of ice, indicating that the metastable supercooled water has a higher vapour pressure than the stable solid state at a given temperature. It is a general principle, that '*the vapour pressure of the metastable phase is greater than that of the stable phase*'.

The sublimation curve BO and the vapour-pressure curve of the liquid AO have different slopes at the point O.

$$\text{At } 0^\circ\text{C,} \qquad (dp/dT)_{OA} = \frac{L_v}{TV_g} = \frac{607 \text{ cal}}{TV_g}$$

$$(dp/dT)_{OB} = \frac{L_s}{TV_g} = \frac{687 \text{ cal}}{TV_g}$$

Hence the slopes of the two curves would be different.

TWO COMPONENT SYSTEMS

15.6. Liquid-Liquid Phases

Two liquids may be completely miscible in all proportions as in the case of water and alcohol, or they may be immiscible as nitrobenzene and water. But if we add some phenol to water, first phenol will be dissolved in water but as the amount of added phenol increases, phenol will form a separate layer. In fact the water layer will contain dissolved phenol and the phenol layer will also have appreciable amount of dissolved water. Such liquids are *partially miscible*.

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* Pure water actually freezes at 0.0024°C under 1 atmosphere, hence the experimental value of triple point is 0.0075 + 0.0024 = 0.0099°C.

When two such partially miscible liquids (*A* & *B*) are brought together in appreciable amounts we have two saturated solutions in two layers—one of *A* in *B* and another of *B* in *A* — at equilibrium. These two solutions are described as *conjugate solutions*.

The study of miscibility of partially miscible liquid pairs are quite interesting. It is usually convenient to study such miscibilities under the external atmospheric pressure which is taken as constant and much higher than the vapour pressure of the components. Hence, in such studies of miscibility under constant pressure, the vapour phase is ignored. The mutual solubilities of liquids are represented graphically in a temperature-composition diagram.

System : Phenol and Water. In Fig. 15*e*, *AB* is the solubility curve of phenol in water. It gives the percentage of phenol dissolved in water at different temperatures, the solubility rising with temperature. On the other hand when water is added to phenol slowly small amounts of water are immediately dissolved but when the amount of added water is increased, the limit of saturation is reached and water forms a separate layer. The solubility curve of water in phenol is given by *CB*, the solubility again increasing with temperature. The two solubility curves meet smoothly at *B* (temp. 66°C, 33 % phenol).

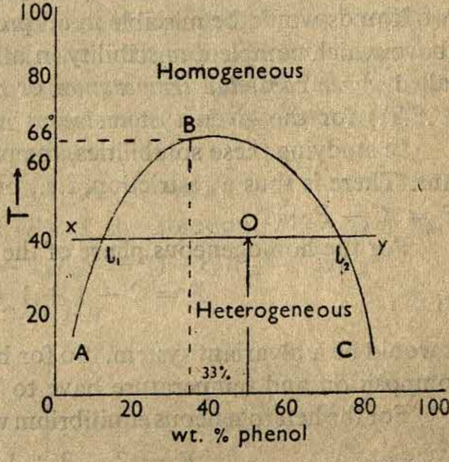


Fig. 15*e*. Water and phenol (miscibility)

At a given temperature (say 40°), if we have *x* percent phenol in water, it will be completely miscible and a homogeneous solution will result. Keeping the temperature constant, if we go on increasing the amount of phenol, the solubility limit l_1 will be reached. Any further addition of phenol will give rise to two separate layers ; (*a*) water in phenol layer and (*b*) phenol in water layer. That is, on the left of l_1 a point will correspond to homogeneous solution and on the right a point would indicate existence of heterogeneous system of two layers or phases. *AB* is thus the boundary between homogeneous and heterogeneous conditions of the system. Similarly at 40°C if we take y percent water in phenol then it would be dissolved fully to produce homogeneous solution. Increased amounts of water, at const. temperature, will lead to the limiting solubility l_2, beyond which two heterogeneous phases of conjugate solutions would appear. That is, any composition indicated by a point within the area ABC will correspond to heterogeneous phases, whereas any composition indicated by a point outside ABC would lead to the occurrence of homogeneous equilibrium.

Thus at 40°C if a mixture of 50% water and 50% phenol be shaken and allowed to settle, the two conjugate solutions will separate : one layer having composition as at l_1 and the other layer with composition as at l_2. The relative amounts of the two layers is given by the ratio, Ol_2/Ol_1.

It is also evident that at any temperature above that of B, the two liquids would be miscible in all proportions. This temperature above which complete miscibility in all proportions takes place is called *upper consolute temperature* or *critical solution temperature* (C.S.T.) for the given system.

In studying these solubilities, the pressure is always kept constant. There is thus a restriction, *i.e.*, one variable is fixed. Hence, $F = C - P + 1$.

For the homogeneous phase of the two component liquids,

$$F = 2 - 1 + 1 = 2$$

It would be a bivariant system. So for homogeneous solutions both composition and temperature have to be defined.

For the heterogeneous equilibrium with two conjugate solutions,

$$F = 2 - 2 + 1 = 1$$

i.e., the system would behave as a univariant one. So if either the temperature or the composition be fixed, the other would be automatically known from the diagram.

At the critical solution temperature (B), there is an additional restriction that composition of the two conjugate solutions must be the same.

Hence $$F = 2 - 2 + 1 - 1 = 0$$

Hence, the point B at the critical solution temperature is a nonvariant point.

Many other liquid pairs behave like phenol-water system showing upper consolute temperatures (C.S.T given in bracket), such as :

(*a*) Aniline/hexane ($t = 59.6°C$) (*d*) Cyclohexane/methyl alcohol ($t = 49°C$)
(*b*) Phenol/isopentane ($t = 63.5°C$) (*e*) Bi/Zinc ($t = 850°C$)
(*e*) CS_2/CH_3OH ($t = 40.5°C$) (*f*) Aniline/water ($t = 167°C$)

15.7. Liquid-Vapour Phase

It was shown in Sec. 10-11 that the vapour pressure of a solvent over its solution is proportional to its mole-fraction (x_i). This is Raoults' Law.

$$p_1 = x_1 p^0_1$$

where p_1 is the vapour pressure of the solution and p^0_1 is the vapour pressure of the pure solvent.

If a mixture of two volatile liquids be taken, both the components would obey Raoult's Law.

Consider a liquid pair *A* and *B* which are volatile and completely miscible and form an *ideal* mixture with mole-fractions x_A and x_B. Their vapour pressures in the pure state are $P_A{}^0$ and $P_B{}^0$. If p_A and p_B denote the partial vapour pressures of the two components in the vapour over the solution, then

$$p_A = x_A P_A{}^0 \qquad p_B = x_B P_B{}^0 \qquad \ldots (15.10)$$

The total vapour pressure (P) of the solution; $P = p_A + p_B$,

$$i.e., P = x_A P_A{}^0 + x_B P_B{}^0 = (1 - x_B)P_A{}^0 + x_B P_B{}^0$$

$$\text{or} \quad P = P_A{}^0 + (P_B{}^0 - P_A{}^0)x_B \qquad \ldots (15.11)$$

It is obvious that p_A, p_B or total pressure P plotted against molefraction of either component, say x_A, would yield linear graphs as in Fig. 15*f*.

In this figure, the solid lines represent the partial pressures of *A* and *B*. The dashed line is the total pressure of the solution at different concentrations. When $x_B = 1$, pure *B* is present, $P = P_B{}^0$; when $x_B = 0$ pure *A* is

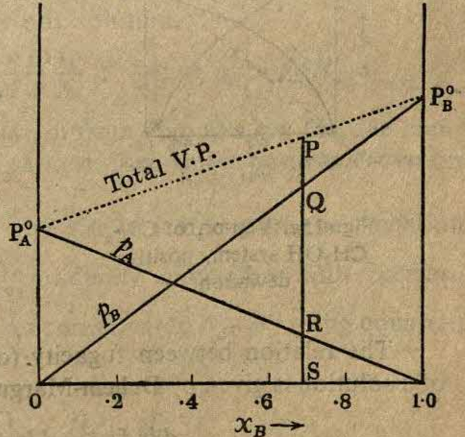


Fig. 15*f*. Vap. Pressures of ideal solutions

present, $P = P_A^0$. And at the conc. $x_B = S$, the total pressure $SP = SR + SQ$.

The equation (15.11) gives the relation between vapour pressure and the composition of solutions.

Such miscible liquid pairs in equilibrium with vapour have two phases and two components. Hence

$$F = C - P + 2 \quad = 2 - 2 + 2 = 2$$

These systems would be bivariant. If the temperature be fixed, the pressure and composition would vary together, *i.e.*, each composition has a definite vapour pressure.

But the Raoults' law is valid only for ideal solutions. In fact, 'ideal solutions' have been conceived on the basis of the Raoults' Law. For real solutions, it is applicable only at very low concentrations. The linearity of the total pressure against composition (Fig. 15*f*) is seldom found. There is often a positive deviation or a negative deviation from the Raoults' law as shown in figs. (15*g* and 15*h*).

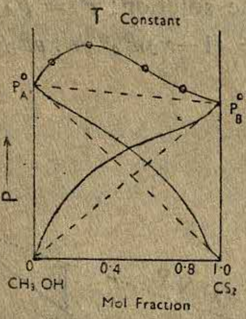
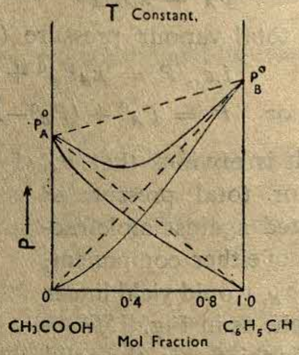


Fig. 15*g*. Vap-pr. of CS_2-CH_3OH system, positive deviation



Fg. 15*h*. Vap-pressure of toluene-acetic acid system, negative diviation

The relation between fugacity (or pressure) and composition of a solution is given by **Duhem-Margules equation** (Sec. 10-9).

$$\frac{d \ln f_1}{d \ln N_1} = \frac{d \ln f_2}{d \ln N_2}$$

In the case of ideal solutions, fugacities may be expressed by partial pressures, hence

$$\frac{d\,ln\,P_1}{d\,ln\,N_1} = \frac{d\,ln\,P_2}{d\,ln\,N_2}$$

From Raoults' Law, $P_1 = N_1 P_1{}^0$, *i.e.*, $\frac{d\,ln\,P_1}{d\,ln\,N_1} = 1$

$$\therefore \quad \frac{d\,ln\,P_2}{d\,ln\,N_2} = \frac{d\,ln\,P_1}{d\,ln\,N_1} = 1$$

Hence, for a solution in which component 1 obeys Raoults' Law at all compositions, the other component will also obey it. This shows that the partial pressures also will bear a linear relationship through the entire composition to the mole-fractions of the components in the mixture. In real solutions, this is seldom found.

(*a*) In real solutions, the deviations from the Raoult's law may be positive or negative. When liquids of different chemical nature are mixed, the solutions generally exhibit positive deviation. When liquids having strong affinities for one another are mixed, the deviation is usually negative.

(*b*) With rise of temperature, the extent of deviation from the Raoult's law diminishes and the liquid solutions approach ideality.

Non-ideal liquid solutions with positive deviation : Since in such a solution, there is a positive deviation,

$$\frac{d \ln \mathbf{f}_1}{d \ln N_1} > 1, \quad i.e., \ \mathbf{f}_1 > \mathbf{f}_1{}^0 N_1$$

If the vapour pressures are not high, $p_1 > p_1{}^0 N_1$

On the other hand, since for any solution,

$$\frac{d \ln \mathbf{f}_2}{d \ln N_2} = \frac{d \ln \mathbf{f}_1}{d \ln N_1}\ ; \quad \text{hence } p_2 > p_2{}^0 N_2$$

Or, if there is a positive deviation from Raoult's law for one component, the second component must also exhibit positive deviation (see Fig. 15*g*).

We further know, that with rise of temperature the deviation decreases. It means that $\frac{\mathbf{f}_1}{\mathbf{f}_1{}^0}$ gradually diminishes with increase in temperature and tends to become equal to N_1. By using equation (10.12), we have

$$\left[\frac{\partial \ln \frac{\mathbf{f}_1}{\mathbf{f}_1{}^0}}{\partial T}\right] = \frac{\bar{H}_1{}^0 - \bar{H}_1}{RT^2},$$

$\bar{H}_1{}^0$ is the partial molar heat-content in the pure state of component 1. As $\frac{f_1}{f_1{}^0}$ diminishes with increase in T, hence $\frac{\bar{H}_1{}^0 - \bar{H}_1}{RT^2}$ must be a negative quantity, or

$$\bar{H}_1 > \bar{H}_1{}^0$$

i.e., partial molar heat-content of the component 1 in solution is greater than the molar heat-content in pure state. Similarly, for the other component, $\bar{H}_2 > \bar{H}_2{}^0$.

Hence, $N_1\bar{H}_1 + N_2\bar{H}_2 > N_1\bar{H}_1{}^0 + N_2\bar{H}_2{}^0$

Or, the heat-content of the solution is greater than the sum of the heat-contents of the components in pure state.

We are thus led to conclude that positive deviation from Raoult's law is observed when solutions are formed from the pure components with absorption of heat. Systems like water-alcohol, ethyl alcohol-heptane, show considerable positive deviation.

Non-ideal liquid solutions with negative deviation : For liquid solutions which deviate negatively from Raoult's Law,

$$\frac{d \ln f_1}{d \ln N_1} < 1, \quad \text{or} \quad f_1 < f_1{}^0 N_1$$

So also, for the 2nd component, $f_2 < f^0{}_2 N_2$.

When one component of a solution shows negative deviation, the other component would also exhibit the same (See Fig. 15*h*).

As in the previous case $\left[\frac{\partial \ln \frac{f_1}{f_1{}^0}}{\partial T}\right] = \frac{\bar{H}_1{}^0 - \bar{H}_1}{RT^2}$

Since with rise of temperature the deviation decreases, so the solution approaches ideality. Hence, $\frac{f_1}{f_1{}^0}$ increases with rise in temperature, and tends to become equal to N_1.

So, $\bar{H}_1{}^0 - \bar{H}_1$ is positive, or $\bar{H}_1{}^0 > \bar{H}_1$.

For the second component also, $\bar{H}_2{}^0 > \bar{H}_2$.

It is obvious that the heat content of the liquid solution is less than the sum of the heat contents of the pure components. We thus arrive at the conclusion that the negative deviation from the

Raoult's law is observed in cases where solutions are formed from the pure components with evolution of heat. Systems like hydrochloric acid and water, ether and chloroform, pyridine and acetic acid, etc. are examples which exhibit negative deviations.

Total vapour pressure and composition of liquid solutions. It is possible to obtain an idea as to how the total vapour pressure of a binary solution would change when the composition in the liquid solution is altered.

Consider a system containing two components 1 and 2 both in the liquid and in the vapour phase. Suppose in the liquid phase, the mole-fractions of the two components are N_1 and N_2 and the mole-fractions in the vapour phase N_1' and N_2'. Let the vapour pressures be denoted by P_1 and P_2. So that the total pressure $P = P_1 + P_2$.

We have,
$$\frac{d \ln \mathbf{f}_1}{d \ln N_1} = \frac{d \ln \mathbf{f}_2}{d \ln N_2}$$

Assuming that vapours behave practically ideally, though the liquid solution may not be so, then
$$\frac{d \ln P_1}{d \ln N_1} = \frac{d \ln P_2}{d \ln N_2}$$

or
$$\frac{N_1}{P_1}\frac{dP_1}{dN_1} = \frac{N_2}{P_2}\frac{dP_2}{dN_2} \qquad \ldots (15.12)$$

or
$$\frac{dP_1}{dN_1} = \frac{N_2 P_1}{N_1 P_2} \cdot \frac{dP_2}{dN_2}$$

Now, $N_1 + N_2 = 1$, or $dN_1 = -dN_2$

and $P = P_1 + P_2$

Hence,
$$\frac{dP}{dN_1} = \frac{dP_1}{dN_1} + \frac{dP_2}{dN_1} = \frac{N_2 P_1}{N_1 P_2} \cdot \frac{dP_2}{dN_2} - \frac{dP_2}{dN_2}$$

$$= \frac{dP_2}{dN_2}\left[\frac{N_2 P_1}{N_1 P_2} - 1\right] \qquad \ldots (15.13)$$

Since $\frac{dP_2}{dN_2}$ is always positive (vapour pressure always rises with increase in its concentration in the liquid), and

if $\frac{N_2 P_1}{N_1 P_2} > 1$; $\frac{dP}{dN_1}$ is positive.

i.e., if $\frac{P_1}{P_2} > \frac{N_1}{N_2}$; $\frac{dP}{dN_1}$ is positive.

But the vapour phase being regarded as ideal ; $\frac{P_1}{P_2} = \frac{N_1'}{N_2'}$

So if $\frac{N_1'}{N_2'} > \frac{N_1}{N_2}$; $\frac{dP}{dN_1}$ is positive.

This means that total vapour pressure (P) will increase with the increase in the mole-fraction of the component which is present relatively in higher proportion in the gas-phase than in the liquid phase. . . . (A)

Again, $\frac{dP}{dN_1}$ is negative, if $\frac{N_1'}{N_2'} < \frac{N_1}{N_2}$

That is, the addition of component which is relatively less in gas-phase than in liquid phase will lower the total vapour pressure. . . (B)

These conclusions (A) and (B) had been embodied empirically by Konowaloff in a general principle from experimental observations. The principle is often mentioned as **Konowaloff's Rule**

In real systems, there is a maximum or a minimum in the vapour pressure curves and at such points $\frac{dP}{dN_1} = 0$. From equation (15.13),

$$\frac{N_2P_1}{N_1P_2} = 1 \quad \text{or} \quad \frac{N_2 . N_1'}{N_1 . N_2'} = 1$$

i.e.,

$$\frac{N_1'}{N_2'} = \frac{N_1}{N_2}$$

That is, in such cirmustances, the composition in the vapour-phase and the liquid phase at equilibrium would be the same.

15.8. Solid-Liquid Equilibria : Eutectic Systems

Eutectic System. A simple binary system consists of two substances, which are miscible in all proportions in the liquid phase but do not chemically react. A mixture of naphthalene and salol will make such a system. Suppose we start with a liquid mixture of 50% naphthalene (m.p. 80°) and 50% salol (m.p. 42°) initially, say at 70°C(x), kept in a closed chamber in vacuum. There will be one vapour phase containing small amounts of the vapours of the two constituents in equilibrium. Under such conditions, $C = 2$ and $P = 2$. So the number of the degrees of freedom is 2. It means that if the composition and the temperature be fixed arbitrarily, the vapour pressure is defined. If the system be now progressively cooled, a solid phase of pure naphthalene would separate at a temperature 60°C nearly. There are now three phases. The degree of variance would now be unity, for $C = 2, P = 3$. In other words, at any given composition, there can be only one temperature when the three phases would co-exist. Conversely, for any given temperature, there would be a fixed composition of the system.

If the system be kept under a constant pressure (say atmospheric pressure, which is much higher than the vapour pressures of the constituents), the pressure variable is restricted. We may now consider only two phases, the solid and the solution. On further cooling of the system, more and more solid naphthalene separates and the composition of the liquid-phase will alter. The equilibrium temperature, or more commonly called the freezing temperature, will vary with the alteration of the composition. From cooling-curve study, we can determine the freezing temperatures of the systems with different compositions. Plotting these, we get a phase-diagram as in Fig. 15*i*. The curve *AB* represents a univariant system of the co-existing phases—solution and solid naphthalene—under constant pressure.

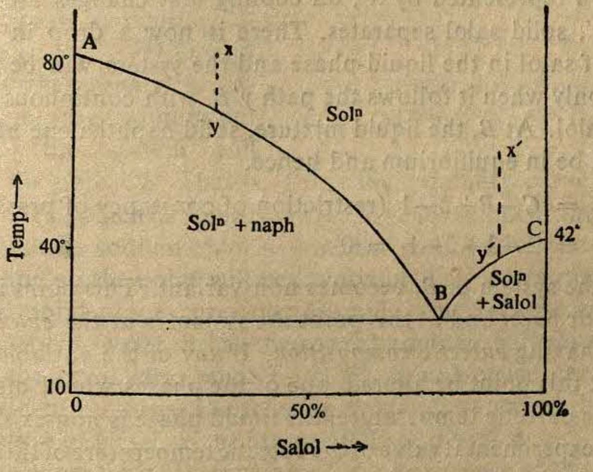


Fig. 15*i*. Phase-diagram of naphthalene-salol system

On the other hand, when a liquid mixture of 10% naphthalene and 90% salol (x′) is progressively cooled, solid pure salol would separate at 35°C approximately at y′. Under the restriction of a constant pressure, solid salol and liquid mixture of a given composition will be in equilibrium at a fixed temperature. On progressive cooling, more and more solid salol would separate and for every composition of the system, there would be a definite temperature. This univariance of the system is represented by the curve *CB*. The two curves intersect at the point *B*. All points lying above the curve *ACB* represent conditions under which only the solution-phase exists. If a solution represented by the point *x* be cooled, the temperature falls but the composition of the liquid remains the same. At the point *y*, crystals of naphthalene separate and the concentration of salol in the solution begins to increase. The system can now only exist in equilibrium when the state of the system follows the curve *yB*. That is, as more and more naphthalene separates, the freezing temperature changes along *yB*. Similarly, a solution represented by *x*′, on cooling first changes along *x*′*y*′, and at *y*′, solid salol separates. There is now a drop in concentration of salol in the liquid-phase and the system will be in equilibrium only when it follows the path *y*′*B*, with continuous separation of salol. At *B*, the liquid mixture, solid naphthalene and solid salol will be in equilibrium and hence,

$$\begin{aligned} F &= C-P+2-1 \text{ (restriction of constancy of pressure)} \\ &= 2-3+2-1 = 0 \end{aligned}$$

That is, the system at *B*, becomes non-variant. This point is called the *eutectic point* and at this point the system is at the *eutectic temperature* having *eutectic composition*. If any of the variables of the system at this point be altered, one of the phases would disappear. Below the eutectic temperature, the liquid phase is non-existent.

The experimental value of the eutectic temperature of this system is 25.49°C with a composition of 22% naphthalene. If we assume the validity of the laws of the ideal solutions in this mixture, then,

$$\log N_1 = -\frac{\triangle H_f}{2.303\,R}\left[\frac{1}{T}-\frac{1}{T_0}\right]$$

The latent heat of fusion of naphthalene is given by, $\triangle H = -2375 + 38.10T - 0.053T^2$. Accepting the experimental value of N_1, the eutectic temperature calculated with the above formula, is found to be 24.7;C. This shows the system is only slightly non-ideal.

(*b*) *Aqueous salt solution.* The most common binary system of this type is that of common salt and water. The phase-diagram of this system under constant atmospheric pressure, at low temperature, is given in Fig. 15*j*. In cooling a very dilute solution the crystals of pure ice separate, whereas if a solution containing a little more than 30% common salt is cooled, the salt separates as dihydrate crystals, NaCl, $2H_2O$. That means, when a solution represented by 'a' is cooled, it would give ice crystals when the point '*b*' is reached and then the equilibrium will shift along the freezing point curve *AB*. Again, if a solution represented by 'a″ be cooled, the solid phase separating at '*b*″ will be NaCl, $2H_2O$, and with further separation of the same, the equilibrium state of the system will follow the path *CB*. That is, *CB* is the solubility curve of NaCl, $2\,H_2O$. At *B*, which has been found to have the temperature (−21°C), ice, dihydrate sodium chloride and the solution will be in equilibrium and so the point will be invariant. This corresponds to the eutectic point of our previous example and because one of the components is water, it has the special name of '*Cryohydric point*'. Below the cryohydric point (−21°C), liquid phase cannot exist. It is evident then that the freezing point of water can be lowered by addition of NaCl, to the extent of 21° at the most.

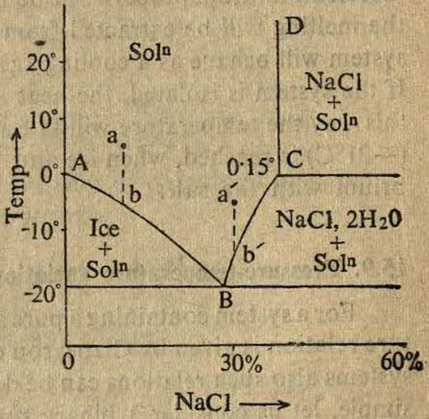


Fig. 15*j*. The phase-diagram of the system (NaCl and H_2O)

The upper limit of temperatue for the existence of the dihydrate salt is + 0.15°C. Above this temperature, there is the transition to the anhydrous state

$$NaCl,\ 2H_2O \rightleftharpoons NaCl + 2H_2O$$

If a more concentrated solution of the salt be cooled then only anhydrous NaCl solid will separate, the solubility curve of the anhydrous salt runs along *CD*.

The behaviour of this system as a common freezing mixture can be easily understood. Suppose we add some salt to ice and water at about – 5°C. The water will dissolve some of the salt and ice will no longer be in equilibrium with the solution. Some of the ice will melt to dilute the solution. This, in turn, will dissolve more salt and the process will be repeated. The heat required for the melting will be extracted from the surroundings and thus the system will behave as a cooling agent for the neighbouring system. If the system is isolated, the heat will be extracted from itself. In this way the temperature will fall until the cryohydric temperature (–21°C) is reached, when ice and the solution can exist in equilibrium with the salt.

15.9. Pressure-temperature variation in binary systems

For a system containing a pure substance, the pressure-temperature relation is given by Clapeyron equation. For multi-component systems also such relations can be deduced. To make the treatment simple, let us consider a binary system present in three phases in equilibrium. Suppose the system contains a saturated solution of a salt in contact with a solid phase of the pure salt and a gas phase containing the vapour of the solvent. The salt is non-volatile.

Let the functions relating to the salt be denoted by the suffix '*a*' and those of the solvent by '*b*'. Further, the solid phase and the gas phase are indicated by single and double primes respectively, whereas the solution phase will be without any prime.

Suppose the system undergoes a change *dT* in temperature with a pressure-change *dP*. In consequence let n_a moles of solid phase pass into the solution and, in order to retain equilibrium, n_c moles of vapour are transferred into the solution phase. The changes in the chemical potentials of the salt will be given by :

(i) in the solution phase,

$$d\mu_a = \frac{\partial \mu_a}{\partial T}\, dT + \frac{\partial \mu_a}{\partial P}\, dP + \frac{\partial \mu_a}{\partial n_a}\, dn_a$$

$$= -\, \bar{S}_a dT + \bar{V}_a dP + \frac{\partial \mu_a}{\partial n_a}\, dn_a$$

(ii) in the solid phase, remembering solid phase is pure salt,

$$d\mu_a' = \frac{\partial \mu_a'}{\partial T} dT + \frac{\partial \mu_a'}{\partial P} dP$$

$$= -S_a'dT + V_a'dP$$

Under conditions of equilibrium, the chemical potentials of the salt in the solution and the solid phases will be equal and hence changes in the same must also be equal, *i.e.*, $d\mu_a = d\mu_a'$. Equating (i) and (ii), we have

$$\text{(iii)} \quad -(\bar{S}_a - S_a')\,dT + (\bar{V}_a - V_a')dP + \left(\frac{\partial \mu_a}{\partial n_a}\right) dn_a = 0$$

Exactly in the same way, for the transfer of dn_2 moles of vapour from the gas to the solution phase, we have

$$\text{(iv)} \quad -(\bar{S}_b - S_b'')dT + (\bar{V}_b - V_b'')dP + \left(\frac{\partial \mu_b}{\partial n_b}\right) dn_b = 0$$

Multiplying (iii) by n_a and (iv) by n_b and adding,

$$\text{(v)} \quad -n_a(\bar{S}_a - S_a')dT + n_a(\bar{V}_a - V_a')dP + n_a\left(\frac{\partial \mu_a}{\partial n_a}\right)dn_a$$

$$-n_b(\bar{S}_b - S_b'')dT + n_b(\bar{V}_b - V_b'')dP + n_b\left(\frac{\partial \mu_b}{\partial n_b}\right) dn_b = 0$$

Now $\quad n_a\left(\frac{\partial \mu_a}{\partial n_a}\right) dn_a + n_b\left(\frac{\partial \mu_b}{\partial n_b}\right) dn_b$

$= n_a d\mu_a + n_b d\mu_b = 0$, from Gibbs-Duhem relation.

Therefore, the equation (v) can be rewritten as,

$$[n_a(\bar{V}_a - V_a') + n_b(\bar{V}_b - V_b'')]dP = [n_a(\bar{S}_a - S_a') + n_b(\bar{S}_b - S_b'')]dT$$

$$\text{or} \quad \frac{dP}{dT} = \frac{n_a\bar{S}_a + n_b\bar{S}_b - (n_a S_a' + n_b S_b'')}{n_a\bar{V}_a + n_b\bar{V}_b - (n_a V_a' + n_b V_b'')}$$

in which the numerator on the right-hand side is the net-change in entropy and the denominator the net-change in volume.

$$\therefore \quad \frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

The measurable heat and volume effects will thus enable us to determine the pressure-change on variation of temperature along the three-phase equilibrium. The equation is quite similar to that of Clapeyron. Such treatment may also be extended to other multicomponent systems.

15.10. Displacement of equilibrium

Suppose in a heterogeneous system of several phases, we have a chemical reaction,

$$A_1 + A_2 \rightleftharpoons A_3 + A_4$$

Further assume that there is phase equilibrium, but an infinitesimal chemical reaction takes place. Then, if x be the degree of reaction, the Gibbs potential change,

$$dG = VdP - SdT + (\mu_3 + \mu_4 - \mu_1 - \mu_2)dx$$

μ-terms are the chemical potentials of the components.

$$\text{At eqm, } (dG/dx)_{T,P} = \mu_3 + \mu_4 - \mu_1 - \mu_2$$

When both chemical and phase eqm. exist, $dG/dx = 0$.

Suppose now, the system shifts to a slightly different eqm, changing the pressure by dP and temperature by dT. The degree of reaction will also change. But $d(dG/dx) = 0$, *i.e.*, change in dG/dx would be nil.

Remembering, G being a function of x, P and T, we have

$$d\left(\frac{dG}{dx}\right) = \frac{\partial^2 G}{\partial x^2}dx + \frac{\partial^2 G}{\partial P \partial x}dP + \frac{\partial^2 G}{\partial T \partial x}dT$$

$$= \frac{\partial^2 G}{\partial x^2}dx + \frac{\partial}{\partial x}\left(\frac{dG}{\partial P}\right)dP + \frac{\partial}{\partial x}\left(\frac{\partial G}{\partial T}\right)dT$$

$$= \frac{d^2 G}{\partial x^2}dx + \frac{\partial V}{\partial x}dP - \frac{\partial S}{\partial x}dT = 0$$

$$\therefore \frac{\partial^2 G}{\partial x^2}dx = \frac{\partial S}{\partial x}dT - \frac{\partial V}{\partial x}dP$$

$$\text{or } \left(\frac{\partial x}{\partial T}\right)_P = \left[\frac{\partial S/\partial x}{\partial^2 G/\partial x^2}\right]_{T,P} = \left[\frac{\partial Q/\partial x}{T(\partial^2 G/\partial x^2)}\right]_{T,P} \qquad \text{. . . (A)}$$

$$\text{And } \left(\frac{\partial x}{\partial P}\right)_T = -\left[\frac{\partial V/\partial x}{\partial^2 G/\partial x^2}\right]_{T,P} \qquad \text{. . . (B)}$$

Since at eqm, G is minimum, hence $\partial^2 G/\partial x^2$ is always positive. Eqn. (A) shows that increase of temp. will cause a reaction to move in a direction where heat absorption will occur. Eqn. (B) shows that an increase of pressure will cause a reaction to follow the path so that volume would decrease.

Problems

1. Establish the *Phase Rule*.

What maximum number of phases can remain in equilibrium in a two-component system? Illustrate.

How many independent components are present in the following systems: (*i*) $Ca(HCO_3)_2$ at high temp. (*ii*) graphite and diamond (*iii*) mixture of Zinc oxide and carbon at higher temperatures.

2. Show that in the $P-T$ phase diagram for water, the three curves shall meet at the same point (Triple point).

3. Two volatile liquids A and B form an ideal homogenous mixture at a constant temperature. Show that the mole-fraction (N_A) of the component A in the liquid and the gas phases would be given by

$$N^l_{\mathrm{A}} = \frac{P-P^{\circ}_{\mathrm{A}}}{P^{\circ}_{\mathrm{A}}-P^{\circ}_{\mathrm{B}}} \text{ and } N^g_{\mathrm{A}} = \left(\frac{P^{\circ}_{\mathrm{A}}}{P}\right)\left(\frac{P-P^{\circ}_{\mathrm{A}}}{P^{\circ}_{\mathrm{A}}-P^{\circ}_{\mathrm{B}}}\right), \text{ where } P = \text{total pressure.}$$

4. Bismuth (*m.p.* 546°K) and Cadmium (*m.p.* 596°K) form homogeneous mixture in the molten state. The eutectic point of this system is $N_{Bi} = 0.45$ mole-fraction, $T_{eu} = 413$°K. Compute the latent heat of fusion of cadmium.

5. Explain with examples : (*a*) Triple point (*b*) Critical solution temperature (*c*) Eutectic point.

What is meant by an invariant point? Are these invariant?

6. The vap. pressures of pure methanol and ethanol at 20°C are 88.7 mm and 44.5 mm. What will be the total pressure over a mixture of the two containing 40% methanol by weight. Also give the composition of the vapour phases. **Ans.** 66 mm. ; 57·1% methanol by wt.

7. The vapour phase over a mixture of benzene and toluene at 80°C contains 70 mole percent of toluene. What is the composition of the liquid phase in eqm. with this? At 80°C, $p^0_{\text{benzene}} = 753$ mm. $p^0_{\text{toluene}} = 290$ mm.

8. When toluene is added to acetic acid, there is an appreciable evolution of heat. Would you expect the vapour phase of the mixture to conform to Raoult's law? If not, what deviations you expect and why?

CHAPTER 16

THE COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

The dilute solutions having low concentrations of the solute tend to behave ideally and obey Raoult's Law. The addition of a solute lowers the free energy of the solution and we shall see other properties are affected; the vapour pressure is lowered, the boiling point is raised, the freezing point is depressed, etc. The extent of these changes brought about in the solution is dependent only on the number of solute particles. Such properties of the solutions which depend on the number of particles are called *colligative* properties.

16.1. Lowering of vapour pressure of Solutions

Consider a *dilute* solution of a non-volatile solute dissolved in a liquid solvent. The parameters of the solvent are denoted by suffix 1 and those of the solute with suffix 2. The mole fraction of the solvent is x_1.

From Raoult's Law, $p_1 = x_1 p_1^\circ$

where p_1 and p_1° are the vapour pressures of the solution and the solvent respectively.

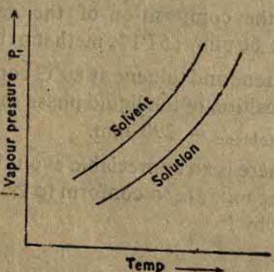


Fig. 16a. Vap-pressure and temperature of pure solvent and solution

Since x_1 is less than 1, hence p_1 is always less than p_1°. That is, *the presence of the solute will always lower the vapour pressure of the solvent.*

It is also a common knowledge that the vapour pressure of the solvent over the pure solvent or over the solution always increases with rise in temperature (Clapeyron equation). These are graphically presented in Fig. 16*a*.

Rewriting Raoult's Law,

$$p_1 = (1-x_2)p_1^\circ$$

where x_2 is the mol-fraction of the solute.

Therefore $\dfrac{p_1^\circ - p_1}{p_1^\circ} = x_2$; *i.e,* $\dfrac{\triangle p}{p_1^\circ} = x_2$ ... (16.1)

Raoult's law, in this form, may be stated as that *in dilute solutions the relative lowering of vapour-pressure of the solvent is equal to the mol-fraction of the solute.*

$$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2}$$

n_1, n_2 are the gm-moles of solvent and solute respectively. For a dilute solution, $n_1 \gg n_2$, hence

$$\frac{\triangle p}{p_1^0} \approx \frac{n_2}{n_1} \qquad \text{... (16.2)}$$

For a definite quantity of a given solvent, n_1 and p_1^0 are both constants,

$$i.e., \ \triangle p \propto n_2$$

which means that *equimolecular quantities of any non-volatile solute dissolved in the same quantity of the same solvent will produce the same lowering of vapour pressure.* This indeed is a direct consequence from the Raoult's law. The lowering of vapour-pressure is thus a colligative property as it depends only on the amount of the solute *i.e.*, the number of molecules and not on their nature.

16.2. Osmotic Pressure of Solutions

Suppose a solution A is kept separated from the pure solvent B by the semipermeable membrane X as in Fig. 16*b*.

The concentration of the solvent is x_1 mol-fraction and that of the solute x_2 mol-fraction. The temp. is kept constant throughout.

Let the pressure initially over both the solvent and the solution be P_0.

μ_1^0 = chemical potential of the solvent in the pure state under pressure P_0 and μ_1 = chemical potential of the solvent in the solution under the same pressure P_0.

In order just to prevent osmosis, the pressure over the solution is raised to P. Then, the osmotic pressure (π) is

$$\pi = P - P_0 \qquad \ldots (i)$$

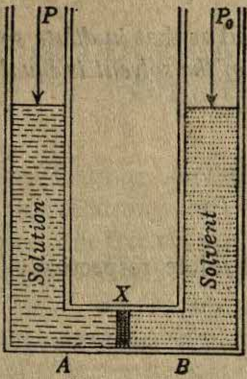


Fig. 16b
Osmotic Pressure

Let $\mu_{1(s)}$ be the chemical potential of the solvent in the solution under pressure P. At-equilibrium, the chemical potentials of the solvent in the solution and in pure state must be the same, *i.e.*,

$$\mu_{1(s)} = \mu_1{}^0 \qquad \ldots (ii)$$

Now, under the pressure P_0, the chemical potential ($\mu_1{}^0$) of the pure solvent is changed to μ_1 due to the presence of solute (eqn. 9.21).

Hence $\mu_1 = \mu_1{}^0 + RT\, ln\, x_1$ ... (*iii*)

Again, in the given solution, the chemical potential of the solvent is μ_1 under pressure P_0 and it changes to $\mu_{1(s)}$ under pressure P, hence

$$\mu_{1(s)} = \mu_1 + \int_{P_0}^{P} \left(\frac{\partial \mu_1}{\partial P}\right)_T dP = \mu_1 + \int_{P_0}^{P} \left(\frac{\partial \overline{G}_1}{\partial P}\right)_T dP$$

Since $\left(\frac{\partial \overline{G}_1}{\partial P}\right)_T = \overline{V}_1$, where $\overline{V}_1$ is the molar volume of the solvent which is supposed to remain the same in dilute solutions,

We have, $$\mu_{1(s)} = \mu_1 + \int_{P_0}^{P} \overline{V}_1 dP$$

or $$\mu_{1(s)} = \mu_1 + \overline{V}_1(P - P_0) = \mu_1 + \overline{V}_1\pi \qquad \ldots (iv)$$

Substituting (*iii*) in (*iv*),

$$\mu_{1(s)} = \mu_1{}^0 + RT\, ln\, x_1 + \overline{V}_1\pi$$

But from (*ii*), $\mu_{(s)} = \mu_1{}^0$, hence, $\pi\overline{V}_1 + RT\, ln\, x_1 = 0$

or $$\pi\overline{V}_1 = -RT\, ln\, x_1 = -RT\, ln\,(1 - x_2)$$

As in dilute solution, x_2 is small, $ln\,(1 - x_2) \approx -x_2$

$$\therefore \qquad \pi\overline{V}_1 = RTx_2 \qquad \ldots (16.3)$$

Rewriting, $$\pi = \frac{RT}{\bar{V}_1}\frac{n_2}{n_1+n_2} \approx \frac{RT}{\bar{V}_1}\cdot\frac{n_2}{n_1} = RT\frac{n_2}{v}$$

where v = total volume of the solvent and n-terms are the respective gm-moles.

Therefore, $$\pi = RTc_2 \qquad \ldots (16.4)$$

where c_2 is the molar concentration of the solute.

The osmotic pressure thus depends on the concentration only at a given temperature, *i.e.*, on the number of molecules. It is thus a colligative property. The equation (16.4) has to be modified if the solute be an electrolyte as the number of particles in solution increases due to dissociation.

16.3. Effect of temperature on the composition in different phases

Consider a liquid solution in equilibrium with its vapour. If the temperature of the system be altered, the composition of both the phases will be affected. But in any given temperature, the fugacity of any component must be the same in both the phases. To take a simple case, let us consider a binary solution with both the components 1 and 2 in the liquid as well as in the gas phase. The different functions of the system may be denoted as follows :

	Mole-fraction in		Fugacity in		Partial Molal Heat content in	
	Liquid	Gas	Liquid	Gas	Liquid	Gas
Component 1	N_1'	N_1''	f_1'	f_1''	$\bar{H}_1'$	$\bar{H}_1''$
Component 2	N_2'	N_2''	f_2'	f_2''	$\bar{H}_2'$	$\bar{H}_2''$

One, two and three primes are used to indicate liquid, gas and solid phases respectively.

Now when the temperature is raised by dT, the composition in both the phases will alter. Let us take any one component (say, component 1), then the change in fugacity of the component in logarithmic form in the two phases would be,

$$d\ln \mathrm{f}_1' = \left(\frac{\partial \ln \mathrm{f}_1'}{\partial T}\right)_{P,N_1'} dT + \left(\frac{\partial \ln \mathrm{f}_1'}{\partial N_1'}\right)_{P,T} dN_1'$$

$$d\ln \mathrm{f}_1'' = \left(\frac{\partial \ln \mathrm{f}_1''}{\partial T}\right)_{P.N_1''} dT + \left(\frac{\partial \ln \mathrm{f}_1''}{\partial N_1''}\right)_{P,T} dN_1''$$

Under conditions of equilibrium, the two expressions are equal to one another. Therefore,

$$\left(\frac{\partial \ln \mathrm{f}_1''}{\partial N_1''}\right)_{P,T} dN_1'' - \left(\frac{\partial \ln \mathrm{f}_1'}{\partial N_1'}\right)_{P,T} dN_1' = \left(\frac{\partial \ln \mathrm{f}_1'}{\partial T}\right)_{P,N_1'} dT - \left(\frac{\partial \ln \mathrm{f}_1''}{\partial T}\right)_{P,N_1''} dT \qquad \ldots (16.5)$$

The variation of fugacity with temperature is given by

$$\left(\frac{\partial \ln \mathrm{f}}{\partial T}\right)_P = \frac{H^0 - H}{RT^2}, \text{ (see eqn 10.12)}$$

Substituting this, we may write,

$$\left(\frac{\partial \ln \mathrm{f}_1''}{\partial N_1''}\right)_{P,T} dN_1'' - \left(\frac{\partial \ln \mathrm{f}_1'}{\partial N_1'}\right)_{P,T} dN_1' = \left[\frac{H_1{}^0 - \bar{H}_1'}{RT^2} - \frac{H_1{}^0 - \bar{H}_1''}{RT^2}\right] dT$$

$$= \frac{\bar{H}_1'' - \bar{H}_1'}{RT^2}\, dT$$

in which $\bar{H}_1'$ and $\bar{H}_1''$ are the partial molal heat contents of the 1st component in the two given phases and $H_1{}^0$ is the molal heat content of the component in the standard state. This relation will hold true whether the different phases, liquid or gas, behave ideally or not. Obviously, $(\bar{H}_1'' - \bar{H}_1')$ is the molal heat of vaporisation of the component 1 in solutions approaching ideality, (i.e., very dilute solution). So,

$$\left(\frac{\partial \ln \mathrm{f}_1''}{\partial N_1''}\right)_{P,T} dN_1'' - \left(\frac{\partial \ln \mathrm{f}_1'}{\partial N_1'}\right)_{P,T} dN_1' = \frac{\triangle H_b}{RT^2}\, dT \qquad \ldots (16.6)$$

A similar equation for the other component will also hold true.

On the other hand, if a binary solution be in equilibrium with a solid phase containing solid solution of the two components, then proceeding in the same fashion, we should have,

$$\left(\frac{\partial \ln \mathrm{f}_1'}{\partial N_1'}\right)_{P,T} dN_1' - \left(\frac{\partial \ln \mathrm{f}_1'''}{\partial N_1'''}\right)_{P,T} dN_1''' = \frac{\triangle H_f}{RT^2}\, dT \qquad \ldots (16.7)$$

$\triangle H_f$ = molal heat of fusion of component 1.

N_1''' = mole-fraction of component 1 in the solid phase

f_1''' = fugacity of component 1 in the solid phase.

Let us now impose the restriction that both the gas and liquid solution phases are ideal. Then, at constant pressure,

$$\mathbf{f}_1' = \mathbf{f}_1^{0\prime} N_1' \text{ and } \mathbf{f}_1'' = \mathbf{f}_1^{0\prime\prime} N_1''$$

or $$d \ln \mathbf{f}_1' = d \ln N_1' = \frac{dN_1'}{N_1'}$$

or $$\frac{d \ln \mathbf{f}_1'}{dN_1'} = \frac{1}{N_1'}$$

Similarly, $$\frac{d \ln \mathbf{f}_1''}{dN_1''} = \frac{1}{N_1''}, \text{ and } \frac{d \ln \mathbf{f}_1'''}{dN_1'''} = \frac{1}{N_1'''} \qquad \ldots (16.8)$$

Substituting these in equations (16.6) and (16.7), we have in *ideal* cases, at constant pressure,

(*i*) Solution-gas systems,

$$\frac{dN_1''}{N_1''} - \frac{dN_1'}{N_1'} = \frac{\triangle H_b}{RT^2}\, dT$$

or $$\left(\frac{\partial \ln N_1''/N_1'}{\partial T}\right)_P = \frac{\triangle H_b}{RT^2} \qquad \ldots (16.9)$$

(*ii*) Solution-solid phase systems,

$$\left(\frac{\partial \ln N_1'/N_1'''}{\partial T}\right)_P = \frac{\triangle H_f}{RT^2} \qquad \ldots (16.10)$$

16.4. Elevation of Boiling point of Solutions

It is common experience that when a solute is added to a liquid, the boiling temperature is raised.

In a dilute solution, the solvent component obeys Raoult's Law and behave ideally, we can thus apply to it the relation (16.9). That is,

$$\left(\frac{\partial \ln N_1''}{\partial T}\right)_P - \left(\frac{\partial \ln N_1'}{\partial T}\right)_P = \frac{\triangle H_b}{RT^2}$$

Let us consider the solution at its boiling temperature T, in equilibrium with vapour, and further suppose, the solute is a non-volatile one. That is, the vapour consists of practically pure solvent, or $N_1'' = 1$. Hence, at constant pressure,

$$\left(\frac{\partial \ln N_1'}{\partial T}\right)_P = - \frac{\triangle H_b}{RT^2}$$

Integrating this between T, the boiling-temperature of the solution and T_0, the boiling-temperature of the pure solvent,

$$\ln N_1' = -\frac{\triangle H_b}{R}\left(\frac{1}{T_0}-\frac{1}{T}\right) = -\frac{\triangle H_b}{R}\cdot\frac{T-T_0}{T.T_0}$$

$$\text{or} \quad \ln(1-N_2') = -\frac{\triangle H_b}{R}\cdot\frac{T-T_0}{T.T_0}$$

$\triangle H_b$ is assumed to remain constant in the small temperature range. In a dilute solution, N_2' is very small, hence

$$N_2' = \frac{\triangle H_b}{RT_0^2}\cdot(T-T_0), \quad \text{since } (T.T_0 \approx T_0^2)$$

$$\text{or} \quad T-T_0 = \frac{RT_0^2}{\triangle H_b}N_2'$$

All the quantities on the right-hand side are positive, and hence $(T-T_0)$ is positive. This means the boiling point of the solution is higher than that of the pure solvent. The equation gives the quantitative relation for the elevation of the boiling point to the mol-fraction of the solute in the dilute solution of a non-volatile non-electrolyte.

$$\triangle T_b = \frac{RT_0^2}{\triangle H_b}N_2' = \frac{RT_0^2}{L_v}N_2' \qquad \ldots (16.11)$$

substituting the molal heat of vaporisation $\triangle H_b$ by more familar symbol, L_v.

In a solution in which 'a' gm. of the solute are dissolved in 'b' gm of the solvent, the mol-fraction of the solute,

$$N_2' = \frac{n_2'}{n_1'+n_2'} \approx \frac{n_2'}{n_1'} = \frac{a/M_2}{b/M_1} = \frac{aM_1}{bM_2} \qquad \ldots (16.12)$$

where, M_1 and M_2 are the mol-weights of the solvent and the solute respectively.

$$\therefore \quad \triangle T_b = \frac{RT_0^2}{L_v}\cdot\frac{a\times M_1}{b\times M_2},$$

which may be rewritten as,

$$\triangle T_b = \frac{RT_0^2}{\frac{L_v}{M_1}\cdot 1000}\cdot\frac{a\times 1000}{b\times M_2} = \frac{RT_0^2}{l_v\times 1000}\cdot\frac{\frac{a}{M_2}\times 1000}{b}$$

$$\text{or} \qquad \triangle T_b = K_b.m \qquad \ldots (16.13)$$

where $l_v = \frac{L_v}{M_1}$ = latent heat of vaporisation *per gm*, and

$m = \frac{a \times 1000}{b \times M_2}$ = molality of the solution, (*i.e.*, no. of gm-moles of solute per 1000 gm of solvent.)

For a given solvent, $\frac{RT_0^2}{l_v \times 1000}$ is a constant (T_0 being the boiling point and l_v, the latent heat of the solvent). This constant, denoted by K_b, is called the *molal boiling point elevation constant* of the solvent and is different for different solvents. If the solution is 1 molal (i.e., 1 gm-mole solute per 1000 gm solvent) then $\triangle T_b = K_b$. Therefore, the molal boiling point elevation constant is the elevation of the boiling point of the solution when 1 gm-mole solute is dissolved in 1000 gm of solvent. We can state the law of elevation of boiling point as :

"*The elevation of the boiling temperature of a given solvent due to the presence of a solute is directly proportional to the molal concentration of the solute and is independent of the nature of the solute.*"

It is thus a colligative property, the elevation of the boiling temperature depending only on the number of dissolved solute particles.

16.5. Depression of Freezing point of Solutions

Next we may consider the freezing point of solutions. Suppose a dilute binary solution is in equilibrium with the solid phase at its freezing temperature T. Assuming conditions of ideality for the solvent component in the dilute solution, we may use equation (16.10),

$$\left(\frac{\partial \ln N_1'}{\partial T}\right)_P - \left(\frac{\partial \ln N_1''}{\partial T}\right)_P = \frac{\triangle H_f}{RT^2}$$

where N_1' and N_1'' are the mole-fractions of the solvent in the liquid phase and in the solid phase respectively. If the solute is practically absent at the solid phase, then $N_1'' = 1$. So,

$$\left(\frac{\partial \ln N_1'}{\partial T}\right)_P = \frac{\triangle H_f}{RT^2}$$

Integrating, $\ln N_1' = -\frac{\triangle H_f}{RT} + c$ (constant)

When $N_1' = 1$ (pure solvent), $T = T_0$, the freezing point of the pure solvent.

$$\therefore \quad c = \frac{\Delta H_f}{R} \frac{1}{T_0}$$

Substituting

$$\ln N_1' = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) = -\frac{\Delta H_f}{R} \frac{T_0 - T}{T_0 . T}$$

$$\text{or } \ln(1 - N_2') = -\frac{\Delta H_f}{R} \frac{T_0 - T}{T_0^2} \qquad [\because T . T_0 \approx T_0^2]$$

$$\therefore \quad N_2' = \frac{\Delta H_f}{R} \frac{T_0 - T}{T_0^2}$$

$$\text{or} \qquad \Delta T_f = T_0 - T = \frac{RT_0^2}{\Delta H_f} N_2' = \frac{RT_0^2}{L_f} N_2' \qquad \ldots (16.14)$$

Since the quantities on the right-hand side are all positive, hence $T_0 > T$. That is, the freezing point of the solution is lower than that of the pure solvent. The depression of the freezing point is proportional to the mole-fraction of the solute.

As in the previous section, for a solution containing 'a' gm of the solute in 'b' gm of the solvent, $N_2' = \frac{a.M_1}{b.M_2}$, (eqn 16.11).

$$\text{So that} \qquad \Delta T_f = \frac{RT_0^2}{L_f} . \frac{a \times M_1}{b \times M_2}$$

$$\text{or} \qquad \Delta T_f = \frac{RT_0^2}{l_f \times 1000} . \frac{a \times 1000}{b \times M_2}$$

$$\text{or} \qquad \Delta T_f = K_f m \qquad \ldots (16.15)$$

where $\frac{RT_0^2}{l_f \times 1000} = K_f$, *molal freezing point depression constant* of the solvent, l_f = latent heat of fusion *per gram* of the solvent, and m = molality of the solution.

If $m = 1$, then $\Delta T = K_f$. Hence, the molal freezing point depression constant is the depression of the freezing point of the solution when 1 gm-mole of the solute is dissolved in 1000 gm. of the given solvent.

The law of the depression of the freezing point may then be stated as :

"The depression of the freezing temperature of a given solvent due to the presence of a solute is directly proportional to the molal concentration of the solute and is independent of the nature of the solute."

The depression of the freezing point depends on the concentration of the solute only and hence it is a colligative property.

16.6. Molecular weight determination from the laws of dilute solutions

The dilute solution laws have been quantitatively expressed as :

Law

(*a*) Raoult : $$\frac{P_0-P}{P_0} = \frac{n_2}{n_1} = \frac{a.M_1}{b.M_2}$$

(*b*) Osmotic pressure : $$\pi = cRT = \frac{a}{M_2V}RT$$

(*c*) Boiling-point elevation : $$\triangle T_b = K_b\frac{a\times 1000}{b\times M_2}$$

(*d*) Freezing-point depression : $$\triangle T_f = K_f\frac{a\times 1000}{b\times M_2}$$

where the dilute solution contains '*a*' gm of solute (mol-weight M_2) dissolved in '*b*' gm of solvent (mol-weight M_1) or V litres of solvent, at temperature T.

It is comparatively easy to determine experimentally the lowering of vapour pressure, the osmotic pressure, the boiling point-rise or the freezing-point depression of a given solution. If the quantities of the solute (*a*) and of a known solvent (*b*) are known, the use of the above formulae would enable us to determine the value of M_1, mol-weight of the solute. In text-books of physical chemistry, various methods for the determination of osmotic pressure, vapour-pressure lowering, rise of boiling point or depression of freezing point are given. In fact, the most common practice of determination of the mol-weight of a solute is by determining accurately the freezing-point depression or boiling-point elevation (say, by Beckmann apparatus) and employing equation (*c*) or (*d*) as the case may be.

It is however necessary to know the value of K_b or K_f, the molal elevation or depression constant of a solvent. It can be done in two ways. 'K_b' or 'K_f' can be calculated from the knowledge of the latent heat and the boiling point or melting point of the solvent with equations,

$$K_b = \frac{RT_b^2}{l_v\times 1000}; \quad K_f = \frac{RT_f^2}{l_f\times 1000}$$

Alternatively, the equation $\triangle T_b = K_bm$ (or $\triangle T_f = K_fm$) can also be used. These equations are valid in dilute solutions only, and so the measurement of $\triangle T$ with a molal solution will not be correct. A dilute solution with a definite amount of a *known* solute dissolved in a given amount of a *known* solvent should be taken and the boiling point or freezing point of this solution should be accurately determined. Thus, in equations,

$$\Delta T_b = K_b \frac{a \times 1000}{b \times M_2}, \quad \text{or} \quad \Delta T_f = K_f \frac{a \times 1000}{b \times M_2}$$

all the quantities except K_b or K_f would be known, and thus their values can be easily calculated. Some numerical problems are worked out below to illustrate these. The molal boiling point elevation constant, K_b, and the molal freezing point depression constant, K_f, for some common solvents are listed below:

TABLE : MOLAL ELEVATION CONSTANTS

Solvent	*B.Pt.*	K_b	*Solvent*	*B.Pt.*	K_b
Water	100°C	0.513	Carbon-tetrachloride	76.8	5.02
Ethyl alcohol	78.3	1.2	Benzene	80.0	2.6
Acetone	56.0	1.7	Acetic acid	118	2.52
Chloroform	61.0	3.85			

TABLE : MOLAL DEPRESSION CONSTANTS

Solvent	*F.Pt.*	K_f	*Solvent*	*F.Pt.*	K_f
Water	0°C	1.86	Nitrobenzene	5.6	6.99
Acetic acid	16.5	3.9	Cyclohexane	6.5	20.2
Benzene	5.5	5.12	Naphthalene	80.2	7.0

Problem 1. The melting point of phenol is 40°C. A solution containing 0.172 gm acetanilide (C_8H_9ON) in 12.54 gm phenol freezes at 39.25°C. Calculate the freezing point constant and the latent heat of fusion of phenol.

the freezing point depression, $\Delta T = 40 - 39.25 = 0.75$

mol-weight of solute, acetanilide (C_8H_9ON) $= 135$

Hence, $$K_f = \frac{\Delta T.b.M_2}{a \times 1000} = \frac{0.75 \times 12.54 \times 135}{0.172 \times 1000} = 7.38$$

Since $$K_f = \frac{RT_0^2}{l_f \times 1000} = \frac{2 \times (313)^2}{l_f \times 1000}$$

latent heat of fusion of phenol, $$l_f = \frac{2 \times 313^2}{7.38 \times 1000} = 26.5 \text{ calories per gm}$$

Problem 2. The freezing point of pure benzene = 5.44°C and that of a solution containing 2.092 gm of benzaldehyde in 100 gm of benzene is 4.44°C. Calculate the mol-weight of benzaldehyde, when K_f for benzene is 5.1.

$$\Delta T = \frac{a \times 1000}{b \times M_2} K_f$$

or $$M_2 = \frac{a\times 1000}{b\times \Delta T}K_f = \frac{2.092\times 1000}{100\times(5.44-4.44)}\times 5.1 = 106.6$$

Problem 3. The boiling point of acetic acid is 118.1 °C and its latent heat of evaporation is 121 cal. per gm. A solution containing 0.4344 gm anthracene in 44.16 gm of acetic acid boils at 118.24°C. What is the mol-weight of anthracene?

$$M_2 = \frac{RT_b^2}{l\times 1000}\cdot\frac{a\times 1000}{b\times \Delta T_b}; \qquad (\Delta T_b = 0.14°)$$

$$= \frac{0.002\times(391.1)^2}{121}\cdot\frac{0.4344\times 1000}{44.16\times 0.14} = 178$$

Problem 4. At 100°C the vapour pressure of a solution of 6.5 gm of a solute in 100 gm of water is 732 mm. What is the boiling point of the solution? ($k_b = 0.52$). Assume the laws of dilute solution.

At 100°C, the vapour pressure of pure water $P_0 = 760$ mm.

So $$\Delta P = P_0 - P = 760-732 = 28 \text{ mm.}$$

Hence, $$\frac{n_2}{n_1} = \frac{\Delta P}{P_0} = \frac{28}{760}.$$

Now, $$\Delta T_b = k_b\,\frac{a\times 1000}{b\times M_2} = k_b\cdot\frac{n_2\times 1000}{\frac{b}{M_1}\times M_1}$$

$$= k_b\,\frac{n_2}{n_1}\times\frac{1000}{M_1} = 0.52\times\frac{28}{760}\times\frac{1000}{18} = 1.065°$$

Hence the boiling temperature of the solution, $T = 101.064$°C.

16.7. Abnormal Behaviour of Solutions

The equations derived in the previous sections for osmotic pressure, lowering of vapour pressure, elevation of boiling point etc. for dilute solutions seem not to be valid when the solutes are electrolytes. Much higher values for osmotic pressure, elevation of boiling point, etc. are obtained by using electrolyte solutes. van't Hoff introduced a factor, '*i*', to contain the deviations from the ideal equations in case of solutions of electrolytes, expressing,

$$\pi_{ideal} = C_2RT, \qquad \pi_{observed} = iC_2RT \qquad \ldots (16.16)$$

Therefore, $$i = \frac{\pi_{obs}}{\pi_{theo}} \qquad \ldots (16.17)$$

The *van't Hoff's factor* 'i' is thus the ratio of the observed osmotic pressure and the ideal osmotic pressure.

It was further found that for a given solution of an electrolyte the deviation in any colligative property would be the same as that in osmotic pressure, *i.e.*,

$$i = \frac{\pi_{obs}}{\pi_{theo}} = \frac{\Delta T_{f(obs)}}{\Delta T_{f(theo)}} = \frac{\Delta T_{b(obs)}}{\Delta T_{b(theo)}} = \frac{\Delta p_{obs}}{\Delta p_{(theo)}} \qquad \ldots (16.8)$$

In high dilutions, 'i' tends to the numerical value '*two*' for electrolytes like NaCl, $MgSO_4$, HNO_3, etc. For electrolytes like H_2SO_4, $CoCl_2$ etc. the value approaches '*three*' ; for $K_3Fe(CN)_6$, the value tends to '*four*' and so on.

TABLE : VAN'T HOFF FACTOR 'i' FROM OBS. ΔT_f FOR DIFFERENT ELECTROLYTES

Electrolyte	*Molality*			
	1.00	0.1	0.01	0.001
NaCl	1.81	1.87	1.94	1.97
HCl	2.12	1.89	1.94	1.98
$CuSO_4$	0.93	1.12	1.45	—
HNO_3	1.92	1.89	1.96	1.97
H_2SO_4	2.17	2.12	2.26	2.82
$CoCl_2$	—	2.62	2.75	2.90
$Pb(NO_3)_2$	1.31	2.13	2.63	2.89
$K_3Fe(CN)_6$	—	2.85	3.36	3.82

The explanation of the abnormal colligative properties of solutions of electrolytes comes readily from the Arrhenius dissociation theory. According to the dissociation theory, the electrolyte molecules in solution break up into positive and negative ions. In very high dilutions, the dissociation is complete. Thus in dilute solutions, p molecules of NaCl will give rise to $2p$ ions ; p molecules of H_2SO_4 will give $3p$ ions and so on. Since the colligative properties depend on the units of solute present in solution irrespective of their chemical nature and because, due to ionisation the number increases, the values of the colligative properties observed are much higher. In fact, these results from the dilute solutions gave the strongest and most dramatic support to the Arrhenius theory of dissociation.

Generally speaking, suppose a molecule breaks up into n ions in a given solution of concentration c_2. If α is the degree of dissociation, then

conc. of undissociated molecules $= (1-\alpha)c_2$
and conc. of (dissociated) ions $= n.\alpha c_2$

Hence total conc. of solute particles $= c_2[1 + \overline{n-1}\alpha]$

The osmotic pressure of such a solution, $\pi_{obs} = c_2[1 + (n-1)\alpha]\ RT$

But from eqn. (16.7) van't Hoff's corrected equation is,

$$\pi_{obs} = i.c_2RT$$

Hence $i = 1 + (n-1)\alpha$ or $\alpha = (i-1)/(n-1)$

It is obvious that

$$\triangle T_b = K_b[1 + (n-1)\alpha]m$$
$$\triangle T_f = K_f\ [1 + (n-1)\alpha]m \qquad \text{etc.}$$

Problem. A solution containing 4.13 gm LiCl per litre freezes at $-0.343°$C. Calculate van't Hoff factor and the degree of dissociation.

$$M_{LiCl} = 42.5, \qquad \triangle T_f = 0.343°$$

Calculated $\triangle T_f = k_f.m = 1.86 \times \frac{4.13}{42.5}$

$$\therefore \qquad i = \frac{\triangle T_{f\,obs}}{\triangle T_{f\,theo}} = \frac{0.343\times 42.5}{1.86\times 4.13} = 1.898$$

The degree of dissociation, $\alpha = (i-1)/(n-1) = i-1 = 0.898 = 89.8\%$

Problem. What would be the conc. in gm/litre of a solution of a non-electrolyte ($M = 180$) which would be isotonic with a decinormal solution of sodium chloride, the apparent dissociation of which is 85%?

For NaCl solution $\pi = (1+\alpha)\times 0.1\times RT = 1.85\times 0.1\times RT$
For unknown solute $\pi = cRT = (\omega/180)RT$

where ω gm solute is present per litre.

$\therefore \quad \omega/180 = 0.185, \quad$ or $\quad \omega = 33.3$ gm/litre

Problems

1. Deduce a relation between the vapour-pressure lowering and depression of freezing pt. of a solution due to the presence of a non-electrolyte solute.

2. Establish the relation : $\pi = \frac{\rho RT}{1000\times K_f}\triangle T_f$, for a dilute solution when ρ is the density of the solvent.

3. A mixture of 1 gm naphthalene ($M = 128$) and 10 gm camphor freezes at 147°C, whereas pure camphor freezes at 177.5°C. What is the molal freezing pt. depression constant of camphor?

The m. pt. of a mixture of 1 gm acetainlide and 10 gm camphor is 148.5°C. What is the molecular wt. of acetanilide? Mol. wt. of camphor, 152.

[Ans. 39.04°C, 134.6]

4. At 10°C, the osmotic pressure of a urea solution is 500 mm. The solution is diluted and the temp. is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine the extent of dilution. [Ans. 5 times]

5. The vapour pressure of an aqueous solution of cane sugar ($M = 342$) is 756 mm at 100°C, how many gm of sugar are present in 1000 gm water. Calculate the freezing pt. of the solution also. [Ans. 100.4 gm]

6. The vapour pressure of pure benzene and pure toluene at 86°C are 950 mm and 375 mm respectively. Calculate the composition of an ideal mixture of benzene and toluene which smoothly boils at 86°C.

[Ans. 0.67 mole-fraction of benzene]

7. The b. pt. of ether is 36°C. A solution of 1.6 gm naphthalene ($M = 128$) in 20 gm ether boils at 36.31°C. Calculate k_b and latent heat of vaporisation of ether. [Ans. $k_b = 2.1$, $l = 90.4$ cal]

8. What will be the b. pt of a solution containing 30 gm diphenyl ($M = 154$) in 250 gm benzene? [Given, b. pt. of benzene 80.1°C, $k_b = 2.6$]. [Ans. 82°C]

9. A solution containing 5 gm of an organic solute in 25 gm CCl_4 boils at 81.5°C. What is the mol. wt. of the solute? [b. pt. of $CCl_4 = 77°C$ and $k_b = 5$]

[Ans. 222.2]

10. Heavy water boils at 101.42°C and its molar elevation constant (k_b) is 10% higher than that of pure H_2O.

(*a*) How does its latent heat compare with that of pure H_2O?

(*b*) What will be the vapour pressure of pure D_2O at 100°C if the latent heat of vaporisation be taken as 9960 cal/mole?

11. A sucrose solution has an osmotic pressure of 3 atm at 0°C. What is the vapour pressure of this solution? ($f_{0°C} = 4.579$ mm). [Ans. 4.568 mm]

12. A solution of 3.6 gm A in 150 c.c. water gave an osmotic pressure of 4.48 atm at 17°C. What is the b. pt. of the solution? ($k_b = 0.52$).

[Ans. 100.098°C]

13. Calculate the freezing pt. of 0.111 gm/litre solution of $CaCl_2$ in water ($k_f = 1.86$).

14. The vapour pressure of a solution containing 6.69 gm of $Ca(NO_3)_2$ in 100 gm water is 746.9 mm of Hg at 100°C. What is the degree of dissociation of the salt? (C.U. 1974)

15. Calculate the degree of dissociation in the following aqueous solutions:

(*i*) A 0.01 molal solution of $K_3Fe(CN)_6$ which freezes at −0.06°C

(*ii*) A 0.1 molal solution of AB freezing at − 0.204°C.

[Ans. (*i*) 74.2% (*ii*) 9.7%]

16. A solution containing 0.684 gm cane sugar in 100 gm water freezes at −0.037°C; whereas a solution containing 0.585 gm NaCl in 100 gm water freezes at −0.342°C. Evaluate k_f for water, apparent mol. wt. of NaCl, van't Hoff factor and the percentage dissociation of NaCl in the solution.

[Ans. $k_f = 1.85$, $M_a = 31.65$, $i = 1.848$]

CHAPTER 17

SURFACE PHENOMENON

17.1. Surface Energy

Consider a liquid in contact with its vapour. A molecule in the bulk of the liquid is subjected to forces of attraction from all directions by the surrounding molecules and is practically in a uniform field of force. But for a molecule at the surface, the net attraction towards the bulk of the liquid is much greater than that towards the vapour where the attracting molecules are more widely dispersed. This means that the molecules at the surface are pulled inwards. The result is liquid surfaces in absence of other forces tend to contract to minimum areas. The surface layer seems to behave as a stretched membrane and this psuedomembrane tends to contract. It explains why a small amount of liquid, left freely, such as mercury, rain drop, etc. always takes spherical shape ; becuase the sphere, for a given volume, has the least surface area.

The surface is thus in a state of tension. Any increase in the area of the surface of a liquid against its natural tendency to contract will require performance of work. The amount of work to be done in stretching the surface is obviously proportional to the increased area $\triangle A$.

$$\therefore \qquad W_s = -\sigma \triangle A$$

where σ is called the *surface tension* expressed in dynes-cm^{-1}

Rewriting, $\sigma = -W_s / \triangle A,$

that is the surface tension σ is numerically equal to the surface energy per unit area (expressed in ergs).

The change in energy of a system whose surface area changes by dA may be written as,

$$dU = TdS - PdV + \sigma dA$$

For a reversible, adiabatic, constant-volume change in surface area,

$$\sigma = \left(\frac{\partial U}{\partial A}\right)_{S,V} \qquad \ldots (17.1)$$

On the other hand, σ can be defined in another way. We know, (including work in change of surface),

$$dG = -SdT + VdP + \sigma dA.$$

$$\therefore \quad \sigma = \left(\frac{\partial G}{\partial A}\right)_{T,P} \qquad \ldots (17.2)$$

Hence, surface energy σ is the change in free energy of the system (at const T and P) per unit change in area.

Again at 0°K, $Lt_{T\to 0}\left(\frac{\partial S}{\partial A}\right)_{T,V} = 0$, (Third Law) hence σ will be independent of temperature in the vicinity of 0°K.

Similarly, $\quad dA = -SdT - PdV + \sigma dA$

Using Maxwell-type relation, at const volume, it is easy to show that

$$-\left(\frac{\partial \sigma}{\partial T}\right)_{A,V} = \left(\frac{\partial S}{\partial A}\right)_{T,V} \qquad \ldots (17.3)$$

In increasing the surface, work is to be performed to bring molecules from the bulk to the surface film. If the temperature is raised, thermal energy helps in this transfer and as such less work would be required. That is, σ will decrease with increase in temperature. Since $\left(\frac{\partial \sigma}{\partial T}\right)_{A,V}$ is negative, the entropy (of a pure substance) increases with an isothermal, constant-volume increase in surface area. At the critical temperature $T = T_c$, $\left(\frac{\partial \sigma}{\partial T}\right) = 0$, as the surface disappears.

17.2. Expansion of Surface Film

The increase in the surface-area of a film involves work to be *done* on the system. Consider a minute drop of a liquid having a small surface expanded into a large film in a metal-ring. If σ donetes the surface tension of the liquid and dA be the total increase in surface-area, then work done $w = -\sigma dA$.

From the First Law ; $\quad q = dU + w$

or $\quad TdS = C_A dT - \sigma dA$

assuming, P and V remain unaltered.

Applying the first TdS equation (eqn. 7.1), and substituting P by $-\sigma$ and V by A,

$$TdS_l = C_A dT - T\left(\frac{\partial\sigma}{\partial T}\right)_A dA$$

If the surface be expanded slowly and *isothermally*, then

$$q = TdS = -T\left(\frac{\partial\sigma}{\partial T}\right)_A dA \qquad \ldots \text{(a)}$$

Hence $$dU = q - w = -T\left(\frac{\partial\sigma}{\partial T}\right)_A dA + \sigma dA$$

or $$\frac{dU}{dA} = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_A = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right) \qquad \ldots (17.4)$$

[σ being considered a function of T only]

The left-hand side $\frac{dU}{dA}$ may be defined as the *surface energy per unit area*, which diminishes with rise in temperature and becomes zero in the vicinity of the critical temperature. The variation of surface energy with temperature is represented in Fig. 17*a*.

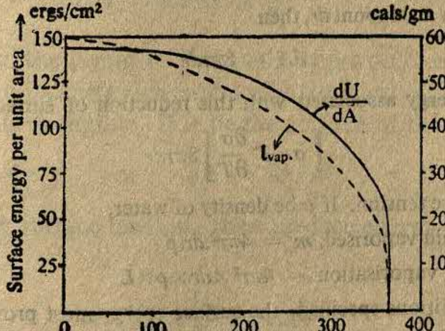


Fig. 17*a*. The variation of surface-energy and latent heat of vaporisation with temperature

The evaporation of a molecule from a liquid is possible only when it possesses energy to overcome the surface energy. As such it is expected that with rise in temperature latent heat of vaporisation would also decrease. In the figure the dotted line (which represents variation of the latent heat with temperature), fulfils the expectation.

As $\left(\frac{\partial \sigma}{\partial T}\right)$ is usually negative then, from equation (*a*) above, it is evident that heat will be absorbed in the isothermal expansion of a film. On the other hand in the sudden adiabatic stretching of a film,

$$C_A dT = T\left(\frac{\partial \sigma}{\partial T}\right) dA$$

or,

$$\frac{dT}{dA} = \frac{T}{C_A}\left(\frac{\partial \sigma}{\partial T}\right) \qquad \ldots (17.5)$$

As the right-hand side is negative, there would be cooling in the adiabatic expansion of a film.

Problem : Given, surface tension of water at 0°C = 76 dynes/cm. and at 30°C = 71.5 dynes/cm., the latent heat of vap. of water at 0°C = 596 cal/gm.

(*a*) Calculate the maximum radius of a drop of water which would evaporate without any heat being supplied to it.

Let r be the radius of the drop.

Its surface area : $A = 4\pi r^2$

Consider a small amount of evaporation from its surface, reducing the radius of the drop by an amount dr, then

$$dA = 8\pi r dr$$

The surface energy associated with this reduction of surface is given by

$$\left[\sigma - T\frac{\partial \sigma}{\partial T}\right] 8\pi r dr$$

where σ is the surface tension. If ρ be density of water,

the mass of liquid vaporised, $m = 4\pi r^2 . dr . \rho$

$\therefore$ The heat of vaporisation $= 4\pi r^2 \times dr \times \rho \times L$

Under the conditions specified, the surface-energy must provide the latent heat of vaporisation.

$$\therefore\ 4\pi r^2 dr \times \rho \times L = 8\pi r dr \times \left[\sigma - T\frac{\partial \sigma}{\partial T}\right]$$

or,

$$r = \frac{2}{L\rho}\left[\sigma - T\frac{\partial \sigma}{\partial T}\right]$$

we know, $\sigma = 76$; $\frac{\partial \sigma}{\partial T} = \frac{71.5 - 76}{30} = -0.15$, $L = 596 \times 4.2 \times 10^7$ ergs.

So, $$r = \frac{2[76 + 273 \times 0.15]}{1 \times 596 \times 4.2 \times 10^7} = 9.35 \times 10^{-9} \text{ cm}$$

(*b*) Show that, when a water film is extended at room temperature isothermally, the amount of heat required is about half the work done in expanding the film.

Let us assume the film be expanded by dA sq. cm at 0°C.

Then the work done $= -\sigma dA = -76\ dA\ ergs$

The heat absorbed $= -T\left(\frac{\partial\sigma}{\partial T}\right) dA = +273 \times (0.15)\ dA = 40\ dA$ ergs,

which is nearly half the amount of work done.

17.3. Vapour Pressure of small drops of liquids

Consider a pure liquid with a flat surface in equilibrium with its vapour a pressure P_1. Also consider a small drop of the same liquid of radius r and let it be in equilibrium with its vapour at a different pressure P_2. The temperature is constant (T) and the vapours may be supposed to behave ideally.

Imagine that a small quantity dn moles of the substance is transferred from the flat surface to the spherical drop. The free energy change involved in this transfer is

$$\triangle G = dn\, RT\, ln \frac{P_2}{P_1}$$

The transfer of the liquid to the small drop would cause an appreciable increase in its surface area, but the decrease of surface area of the flat liquid is negligible. If A be the surface of the drop, then

$$A = 4\pi r^2, \quad \text{or} \quad dA = 8\pi r dr \qquad \ldots \text{(i)}$$

If σ be the surface tension, then the free energy increase in the drop is σdA.

$$\therefore \qquad dn\, RT\, ln \frac{P_2}{P_1} = \sigma dA \qquad \ldots \text{(ii)}$$

If the drop contains n-moles of liquid and if the molar volume of the liquid be V, then the volume of the drop,

$$nV = \tfrac{4}{3}\pi r^3, \quad \text{or} \quad dn = \frac{4\pi}{V} r^2 dr \qquad \ldots \text{(iii)}$$

Substituting (*i*) and (*iii*) in (*ii*)

$$\frac{4\pi r^2}{V} RT\, ln \frac{P_2}{P_1} dr = \sigma . 8\pi r dr$$

or $$RT\,ln\,\frac{P_2}{P_1} = \frac{2\sigma V}{r} = \frac{2\sigma M}{d\times r} \qquad \ldots (17.6)$$

where M and d are the mol. wt and density of the liquid.

Since rt-hand side of the equation is positive, $P_2 > P_1$. That is, the vapour pressure of the small particles is greater than that of the flat surface. As r decreases, the ratio P_2/P_1 will increase. The smaller the particles the greater would be the vapour pressure. This is why large drops grow at the expense of the smaller ones.

Problem : At 0°C, the vapour pressure over a tumbler of water is 4.58 mm. Calculate the vapour pressure of drops of water (at 0°C) with a radius of 10^{-4} mm. The surface tension of water at 0°C is 76 dynes/cm.

Using equation 17.6,

$$\ln\frac{p_2}{p_1} = \frac{2\sigma M}{RTdr}$$

or $$\log p_2 = \frac{2\times 76\times 18}{8.314\times 10^7\times 1.0\times 10^{-5}\times 2.303\times 273} + \log 4.58$$

When $P_2 = 4.669$ mm.

17.4. The Surface Phase Equilibrium

The boundary layer between the two phases, often called the interface, is endowed with many a special property not usually met with in the bulk-phases of the system. For example, the boundary layer has a measurable surface energy. As also it is common experience that often the concentrations of the constituents of the system are higher at the boundary than in the bulk. The surface layer is therefore different from the bulk-phase in its behaviour. In Fig. 17*b*, are represented two phases I and II separated by an interfacial region. The boundaries of the interfacial region are the solid lines XX′ and YY′. It is presumed that the bulk-phase I is

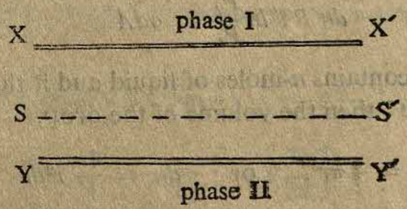


Fig. 17*b*. The surface phase

homogeneous up to the surface XX′ and the bulk-phase II is homogeneous up to the surface YY′. In between XX′ and YY′ the properties of the system vary continuously from purely I-phase to purely II-phase.

The interfacial region can at best be a few molecules thick. Any surface SS′ (represented by the broken line) drawn parallel to XX′ or YY′ in the interfacial region is called a *surface phase*. The surface phase, thus defined, has an area without any thickness. In other words, the surface phase is two-dimensional, the volume being nil.

Let the two bulk-phases and the surface phase in a heterogeneous system be indicated by single prime, double primes and the superscript s. Now if n_i denotes the total gm. mols of a constituent in the system, then

$$n_i = n_i' + n_i'' + n_i^s$$

n_i^s is called the surface excess and it is the difference of the mols of the ith constituent in the surface phase over the amount there would have been if both the bulk-phases were homogeneous right up to the surface SS′. It is, of course, possible to have both positive and negative values for n_i^s.

Many other thermodynamic functions, such as surface energy, surface entropy, surface free energy can be defined in the same fashion ;

Energy, $E = E' + E'' + E^s$

Entropy, $S = S' + S'' + S^s$ etc.

The excess thermodynamic potential, G^s, is then

$$G^s = G - G' - G''$$

where G is the total thermodynamic potential of the system consisting of two bulk-phases and the surface-phase, while G' and G'' are the thermodynamic potentials of the two bulk-phases assuming them to remain homogeneous right up to the layer SS′.

For our convenience, we are considering the surface-phase separately from the bulk-phases. But the surface-phase cannot be distinguished as a physically distinct entity, though the boundary between the two phases exists. It would therefore be necessary to prove that there would be equilibrium of a constituent existing in the bulk-phases and in the surface-phase.

Suppose a system containing several constituents undergoes a small-change in which the different parameters including the surface area s are altered. Then,

$$dG = dG' + dG'' + dG^s$$

Introducing Gibbs-Duhem relation, for the bulk-phases,

$$dG' = -S'dT + V'dP + \mu_1'dn_1' + \mu_2'dn_2' + \ldots + \mu_i'dn_i' \ldots$$

$$dG'' = -S''dT + V''dP + \mu_1''dn_1'' + \mu_2''dn_2'' + \ldots + \mu_i''dn_i'' + \ldots$$

and $dG^s = -S^sdT + \mu_1^sdn_1^s + \mu_2^sdn_2^s + \ldots + \mu_i^sdn_i^s + \ldots + \sigma ds.$

In the last equation for the surface phase, the term V^sdP is ignored as the phase has no volume. But the change in the surface by ds would involve the reversible work σds where σ is the surface tension. This work-term has to be considered in evaluating dG^s. The μ-terms in the equations above are the chemical potentials in the different phases. Adding these equations, we have,

$$dG = -SdT + VdP + \sigma dS + \Sigma\mu_i'dn_i' + \Sigma\mu_i''dn_i'' + \Sigma\mu_i^sdn_i^s$$

where S and V denote total entropy and volume of the system.

It is known that for a system, in equilibrium at a constant temperature and pressure,

$$(dG)_{P,T} = 0.$$

Further, if we consider the system undergoing the change not only at constant temperature and pressure but also with its surface area s unaltered, it can be proved in the same way,

$$(dG)_{P,T,S} = 0.$$

Obviously then under such conditions,

$$(dG)_{P,T,S} = \Sigma\mu_i'\,dn_i' + \Sigma\mu_i''\,dn_i'' + \Sigma\mu_i^sdn_i^s = 0 \quad \ldots (17.7)$$

If we remember that the chemical potentials of a constituent in the two bulk-phases are equal, $\mu_i' = \mu_i''$, and also that for any constituent, $dn_i' + dn_i'' + dn_i^s = 0$, though there is no restriction of a component to pass from one phase to another, then, the solution of the equation (17.7) would give,

$$\mu_i' = \mu_i'' = \mu_i^s \quad \ldots (17.8)$$

That is, the chemical potential of a constituent in the surface-phase and in the bulk-phases must be the same.

17.5 Gibbs adsorption equation

Let us confine our attention to the surface-phase of a heterogeneous system containing several constituents. Suppose the excess surface concentrations of the constituents are denoted by n_1^s, n_2^s, n_3^s . . . etc. The excess thermodynamic potential of the surface-phase would be given by

$$G^s = f(P, T, s, n_1^s, n_2^s \; \ldots\ldots).$$

For a small change of the system,

$$dG^s = \left(\frac{\partial G^s}{\partial P}\right)dP_{T,S,n_1^s\ldots} + \left(\frac{\partial G^s}{\partial T}\right)dT_{P,S,n_1^s\ldots} + \left(\frac{\partial G^s}{\partial s}\right)ds_{P,T,n_1^s\ldots}$$
$$+ \left(\frac{\partial G^s}{\partial n_1}\right)dn_{1\,P,T,S,n_2^s\ldots}^{s} + \left(\frac{\partial G^s}{\partial n_2^s}\right)dn_{2\,P,T,S,n_1^s\ldots}^{s} + \ldots$$

If the change takes place at constant pressure and temperature, and by using equation (17.2), $\sigma = (\partial G/\partial s)_{P,T}$

$$dG^s = \sigma ds + \mu_1^s dn_1^s + \mu_2^s dn_2^s + \ldots \qquad \ldots (A)$$

Since dG^s is a perfect differential,

$$G^s{}_{P,T} = \sigma s + \mu_1^s n_1^s + \mu^s{}_2 n_2^s + \ldots\ldots$$

$$\text{or} \quad dG^s = \sigma ds + \mu_1^s dn_1^s + \mu_2^s dn_2^s + \ldots. + s d\sigma + n_1^s d\mu_1^s + n_2^s d\mu_2^s + \ldots. \qquad \ldots (B)$$

Equating (A) and (B),

$$s d\sigma + n_1^s d\mu_1^s + n_2^s d\mu_2^s + \; \ldots. \quad = 0$$

$$\text{or} \quad d\sigma + \frac{n_1^s}{s}.\, d\mu_1^s + \frac{n_2^s}{s}.d\mu_2^s + \ldots \quad = 0$$

The quantities $\frac{n_1^s}{s}, \frac{n_2^s}{s}, \ldots$ etc. denote the excess surface concentrations of the different constituents per unit area of the surface. These are generally denoted by Γ_1, Γ_2, Γ_3 . . . etc.

Hence

$$d\sigma + \Gamma_1 d\mu_1^s + \Gamma_2 d\mu_2^s + \ldots\ldots\ldots. = 0 \qquad \ldots (17.9)$$

This is the general relation for the equilibrium in the surface-phase.

To take a simple example, let us consider a binary system, say a solution of a solute and a solvent. Then,

$$d\sigma + \Gamma_1 d\mu_1^s + \Gamma_2 d\mu_2^s = 0$$

If the system is in equilibrium at constant surface area(P and T are also constant), the chemical potentials of any constituent will be the same in both the bulk of the solution and the surface, *i.e.*,

$$d\mu_1^s = d\mu_1 ; \qquad d\mu_2^s = d\mu_2$$

Therefore,
$$d\sigma + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 = 0 \qquad \ldots (17.10)$$

If the solution be a dilute one and the surface layer is so chosen that the concentration of the *solvent* in the bulk and the surface-phase be practically the same, (*i.e.*, $\Gamma_1 = 0$), then

$$d\sigma + \Gamma_2 d\mu_2 = 0$$

or
$$\Gamma_2 = -\frac{d\sigma}{d\mu_2} \qquad \ldots (17.11)$$

Γ_2, the excess surface concentration, is really the concentration of the solute adsorbed at the interface per unit area. The chemical potential, μ_2, of the solute in the solution is given by

$$\mu_2 = \mu_2^\circ + RT \ln a_2$$

or
$$d\mu_2 = RT\, d \ln a_2$$

where a_2 is the activity of the solute. The temperature has already been assumed to be constant.

Hence,
$$\Gamma_2 = -\frac{1}{RT}\frac{d\sigma}{d \ln a_2} \qquad \ldots (17.12)$$

Rewriting,
$$\Gamma_2 = -\frac{a_2}{RT}\frac{d\sigma}{da_2} \qquad \ldots (17.13)$$

When the solution is sufficiently dilute to obey the dilute solution laws, $a_2 = c_2$(concentration), the relation may be expressed as

$$\Gamma_2 = -\frac{c_2}{RT}\cdot\frac{d\sigma}{dc_2} \qquad \ldots (17.14)$$

This is *Gibbs adsorption equation.* It correlates the adsorption with the variation of surface tension with concentration. The equation shows that if the surface tension decreases with the increase in concentration (c_2) of the solute (*i.e.*, if $\frac{d\sigma}{dc_2}$ is negative) Γ_2 will be positive or there shall be positive adsorption. On the other hand, there are solutes with which the surface tension rises with increase of concentration of the solute. In these cases, $\frac{d\sigma}{dc_2}$ is positive and so there would be negative adsorption *i.e.*, lesser concentration of the solute in the surface layer compared to that in the bulk-phase.

The exprimental verification of the Gibbs adsorption eqn was first carried out by McC.Lewis. A stream of drops of mercury or hydrocarbon oil were run slowly down a column of an aqueous solution of a dyestuff or caffein. At the surface of the mercury (or oil) drops, the solute was adsorbed. The initial concentration and the final concentration of the solute in the bulk-phase were measured. The difference gave the total amount of solute adsorbed. The total area of the surface of the mercury (or oil) drops were calculated from a knowldge of the total quantity of the mercury and number of drops run down. Thus the value of Γ_2, the adsorbed amount of solute per sq. cm. was known. The right-hand side of the equation (17.14) was also separately determined by directly measuring surface tension at various concentration c_2. The slope of the curve (σ vs. c_2) gave the value of $\frac{\partial\sigma}{\partial c_2}$ and the expression $-\frac{c_2}{RT}.\frac{d\sigma}{dc_2}$ was calculated. The agreement between the two was fairly satisfactory. Later on, Donnan and Barker repeated the experiments with aqueous solutions of nonylic acid and saponin using bubbles of air in place of mercury droplets.

The experimental technique was considerably improved by J. W. McBain. The ends of a narrow trough containing the solution were coated with paraffin, so that the liquid bulged out about 0.05 mm above the vessel without overflow. A swiftly moving microtome was used to slice off the top-layer to be collected in a silver-lined cylinder. The concentration differences in the bulk and surface phases were determined by an interferometer. Solution of different substances, such as common salt, phenol, etc. were taken and the results were found to be in good agreement with the Gibbs equation. An indirect verification of the equation was also obtained from Langmuir's experiments of films of insoluble substances on water.

Problems

1. Calculate the increase in surface energy when a water drop, 0.4 cm in radius, is split up into 125 tiny drops. (σ = 72 dynes/cm). [Ans. 578.6 ergs.]

2. What will be the pressure inside an air bubble (0.1 mm radius) situated just below the surface of water. Given $\sigma = 72$ dynes/cm and pressure is 1.013×10^6 dynes/cm^2 [Ans. 1.0274 dynes/cm^2]

3. Calculate the mean energy required in breaking down one c.c. of water into droplets having mean radius of 10^{-5} cm. Given $\sigma = 72$ dynes/cm. [C.U. 1971]

4. At 25°C, the vap-pressure of water in bulk is 23.76 mm. The surface tension is 72 dynes/cm and molar volume is 18 c.c. What will be the vapour pressure of drops of 2×10^{-5} cm diameter? [Ans. P = 24 mm]

CHAPTER 18

ELECTROMOTIVE FORCE OF VOLTAIC CELLS

18.1. Galvanic Cells

A galvanic cell is a device in which electric energy is obtained in consequence of a chemical reaction occurring within. The cell consists of two electrodes—the positive and the negative—immersed in suitable electrolytes, when an electric potential (ψ) is acquired by each electrode. The electricity is said to flow from the positive to the negative in the external circuit when completed. In fact, the electrons flow from the negative to the positive electrode in the external circuit. The galvanic cell would be a reversible one when with the application of a slightly greater driving force (e.m.f.) from an external source, the chemical reaction may be effected in the opposite direction. In such a reversible cell, each electrode is also reversible, i.e., the changes occurring at the electrodes are also reversible.

To illustrate, let us take the old and familiar Daniell cell in which zinc partially immersed in zinc sulphate solution is the negative electrode and copper in copper sulphate solution is the positive electrode. The reaction is,

$$Zn + Cu^{++} \rightarrow Cu + Zn^{++}$$

Suppose ψ_1 and ψ_2 are the electric potentials acquired by the zinc and copper electrodes respectively. The e.m.f. of the cell (E) is

$$E = \psi_2 - \psi_1 \qquad \ldots (18.1)$$

The manner of the formation of electric potential at an electrode is being conceived in the following way :

A metal is regarded as an assembly of metal ions and free electrons. When the metal is in contact with water, some metal ions enter into the liquid due to a tendency in the metal, called by Nernst as '*electrolytic solution tension*'. As some metal ions leave the solid, the solid becomes negatively charged and the solution positively. In consequence, due to electrostatic force, any further transference of the metal ions is prevented and the ions, attracted by the negatively charged metal, remain near the metal surface forming a double layer. If the metal is placed in a solution containing its own ions, the metal ions from the solution in virtue of their osmotic pressure may enter into the metal rendering its surface positively charged. Again, by attraction now, the anions would flock near the positively charged metal surface and form a double layer. There is thus always a double layer at the contact of the electrode-metal and electrolyte. Hence, a difference of potential exists between the metal phase and the solution phase. This potential difference in the half-cell is called the *single electrode potential.* The transfer of metal ions from the solution to the metal would obviously depend upon the magnitude of the electrolytic solution tension of the metal and the osmotic pressure.

Due to the uncertainty of the physical significance of Nernst's electrolytic solution tension, the electrode potential is at present supposed to be due to the difference in the rates of two opposing processes, namely, the transfer of ions from the metal to the solution and the discharge of ions from the solution on the metal. If the rate of transfer of metal ions into solution be greater, there will be excess of electrons in the metal rendering it negative, which will attract + ve ions forming a double layer. If, on the other hand, the rate of discharge of ions from the solution to the metal be greater than that of the opposite process, the metal would be positive and it will attract negative anions forming a double layer. In any case, a double layer would be formed giving rise to electrical potential difference, which has been called the electrode potential. Similar conditions also apply to the non-metal or other electrodes.

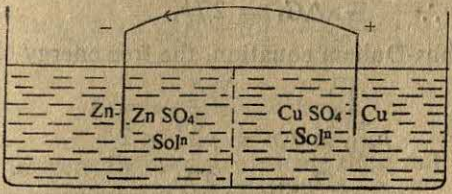


Fig. 18*a*. Daniell cell

With the formation of the double layer, an equilibrium is set up, when the escaping tendency of the metal ions in the solid phase would obviously be equal to the escaping tendency of the metal ions in the solution phase. Thermodynamically, two conditions in such equilibrium must be recognised. Firstly, the chemical potential of M^+ ions in solid and in solution must be equal. Secondly, in the equilibrium

$$M \rightleftharpoons M^+ + e\,; \qquad \mu_M = \mu_{M+} + \mu_e$$

In our Daniell cell, therefore,

$\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{++} + 2e$, we have (*i*) $\mu_{\mathrm{Zn}++}$ (soln) $+ 2\mu_{e(1)}$

Similar will also be the situation at the copper electrode, where

$\mathrm{Cu} \rightleftharpoons \mathrm{Cu}^{++} + 2e$, hence, (*ii*) $\mu_{\mathrm{Cu}} = \mu_{\mathrm{Cu}++} + 2\mu_{e(2)}$

$\mu_{e(1)}$ and $\mu_{e(2)}$ are the chemical potentials of the electrons in the zinc sulphate and in the copper sulphate solutions per gm eqv.

Subtracting (*ii*) from (*i*),

$$\mu_{Zn} - \mu_{Cu} = \mu_{Zn++} - \mu_{Cu++} + 2\mu_{e(1)} - 2\mu_{e(2)}$$

Rewriting, $(\mu_{Cu} + \mu_{Zn++}) - (\mu_{Zn} + \mu_{Cu++}) = -2[\mu_{e(1)} - \mu_{e(2)}]$

or $\quad \Sigma\mu = \mu_{(\text{resultants})} - \mu_{(\text{reactants})} = -2[\mu_{e(1)} - \mu_{e(2)}] \quad \ldots (18.2)$

The left-hand side is really the free energy change of the chemical process occurring in the cell, hence

$$-\Delta G = 2\mu_{e(1)} - 2\mu_{e(2)} \qquad \ldots (18.3)$$

During the chemical process, if 1 gm-mole of zinc dissolves then two faraday ($2\mathcal{J}$) of charge would be transferred across the double layer at the zinc electrode (potential ψ_1). The work involved $= 2\mathcal{J}\psi_1$. This work is equal to the drop in free energy by definition (under reversible condition),

$$\therefore \quad -\Delta G_1 = 2\mathcal{J}\psi_1$$

From Gibbs-Duhem equation, the free energy change is given by

$$\mu_{e(1)} \times \Delta n = \mu_{e(1)} \times 2$$

Hence $\quad 2\mu_{e(1)} = 2\mathcal{J}\psi_1$

Similar is the change in the copper electrode of the cell, so

$$2\mu_{e(2)} = 2\mathcal{J}\psi_2$$

The electrode potentials are opposite in sign, hence

$$2\mu_{e(2)} - 2\mu_{e(1)} = 2\mathcal{J}(\psi_2 - \psi_1) = 2\mathcal{J}E, \text{ (from eqn (18.1).}$$

Substituting this in eqn 18.3,

$$\Delta G = -2\mathcal{J}E$$

The factor 2, indicating the number of gm-eqv. of electrons transferred, may be replaced by *n* in a general process, so that

$$-\Delta G = n\mathcal{J}E \qquad \ldots (18.4)$$

That, is, the output of electric energy ($n\mathcal{J}E$) is equal to the free energy change of the chemical process. The validity of this relation has been amply established from experiments.

In the Daniell cell, the zinc electrode, where zinc gives up its electrons, i.e., oxidation occurs is the negative electrode of the cell. The copper electrode, where copper takes up electrons, i.e., reduction occurs is the positive electrode. The galvanic cell (Daniell's) is represented as,

$$\mathrm{Zn} \mid \mathrm{Zn^{++}}(\text{conc. } c_1) \parallel \mathrm{Cu^{++}}(\text{conc. } c_2) \mid \mathrm{Cu}$$

where vertical lines indicate phase boundaries. The double line is the link between two solutions.

The cell reaction is

$$\begin{array}{c} \mathrm{Zn} - 2e = \mathrm{Zn^{++}} \\ \mathrm{Cu^{++}} + 2e = \mathrm{Cu} \\ \hline \mathrm{Zn} + \mathrm{Cu^{++}} = \mathrm{Zn^{++}} + \mathrm{Cu} \end{array} \qquad \ldots \text{(A)}$$

It is the usual custom to place the negative electrode on the left and the positive electrode on the right while writing. The reaction equation, by convention, is written starting from the left, i.e., with the zinc electrode as in (A) above.

Now $-\triangle G = nJE$, and from Gibbs-Helmholtz relation

$$\triangle G = \triangle H + T\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$$

Hence

$$-nJE = \triangle H + T\left[\frac{\partial(-nJE)}{\partial T}\right]_P$$

or

$$E = \frac{-\triangle H}{nJ} + T\left(\frac{\partial E}{\partial T}\right)_P \qquad \ldots (18.5)$$

This relation is universally used to evaluate the e.m.f. of a cell.

It is further known from equation (6.22) that

$$\triangle S = -\left[\frac{\partial(\triangle G)}{\partial T}\right]_P$$

$$\therefore \qquad \triangle S = -\left[\frac{\partial(-nJE)}{\partial T}\right]_P = nJ\frac{dE}{dT} \qquad \ldots (18.6)$$

We can thus measure the entropy-change from the temperature-coefficient of the e.m.f. of a cell. Hence, the knowledge of the e.m.f. of a cell permits the evaluation of $\triangle S$, $\triangle G$ and also $\triangle H$ of a chemical process (since $\triangle H = \triangle G + T\triangle S$).

To illustrate : Let us take the Clarke cell,

$$\mathrm{Zn} \mid \mathrm{ZnSO_4} \text{ solution } \parallel \mathrm{Hg_2SO_4} \mid \mathrm{Hg}$$

For this cell, $E = 1.420$ volts and $dE/dT = -1.2\times10^{-3}$ volts/°C, at 25°C.
The cell reaction : $\mathrm{Zn} + \mathrm{Hg_2SO_4} = \mathrm{ZnSO_4} + 2\mathrm{Hg}$;
heat of reaction, $\triangle H = -81200$ cal

Now, $\triangle H = -nJE + nJT\dfrac{dE}{dT}$

$$= \frac{-2\times96500\times1.420}{4.2} + \frac{2\times96500}{4.2}\times(273+25)\times(-1.2\times10^{-3})$$

$$= -65250 + (-16710) = -81960 \text{ cal}$$

It is thus obvious that $\triangle H$ is not equal to the output of electrical energy. The electrical energy is equal to $-\triangle G$.

In a rare instance, $\dfrac{dE}{dT}$ is found to be negligibly small, so that $\triangle H = \triangle G = -nJE$. That is, electrical energy is equal to the heat of reaction. This happens in the Daniell cell ($\triangle H = -50300$ cal), and ($nJE = 2\times96500\times1.09/4.2 = 50010$ cal).

Problem. At 25°C, the e.m.f. of the cell

$$\text{Pb} - \text{PbCl}_2 - \text{HCl}(m) - \text{Ag} - \text{AgCl}$$

is 0.49 volts and its temperature coefficient $\dfrac{\partial E}{\partial T} = -1.8\times10^{-4}$ volt/degree. Calculate (*a*) the entropy-change when 1 gm-mole of silver is deposited and (*b*) the heat of formation of silver chloride, if the heat of formation of lead chloride is $H_{PbCl_2} = -86000$ cal

The cell reaction : $\frac{1}{2}\text{Pb} + \text{AgCl} = \text{Ag} + \frac{1}{2}\text{PbCl}_2$

$$\triangle G = -nJE = -\frac{1\times96500}{4.2}\times0.49 = -11260 \text{ cal}$$

And $\triangle S = -\dfrac{\partial(\triangle G)}{\partial T} = nJ\dfrac{\partial E}{\partial T} = \dfrac{96500}{4.2}(-1.8\times10^{-4})$

$$= -4.14 \text{ cal/degree}$$

The heat of reaction of the chemical change,

$$\triangle H = \triangle G + T\triangle S = -11260 + 298\times(-4.14)$$
$$= -12494 \text{ cal}$$

This heat of reaction is the algebraic sum of the heats of formation of the components ;

$$\triangle H = H_{Ag} + \tfrac{1}{2}H_{PbCl_2} - \tfrac{1}{2}H_{Pb} - H_{AgCl}$$
$$= 0 - \tfrac{1}{2}\times86000 - \tfrac{1}{2}\times0 - H_{AgCl}$$

or heat of formation of silver chloride,

$$H_{AgCl} = -\tfrac{1}{2}\times86000 - \triangle H = -30506 \text{ calories/mole}$$

It is known that when a reaction occurs spontaneously $\triangle G$ is negative and hence e.m.f. is positive. If the experimental value or calculated value in a galvanic arrangement e.m.f. is negative, then $\triangle G$ will be positive ; the reaction is not likely to occur spontaneously. For example, if we have a galvanic cell arranged as

$$\text{Ag} \mid \text{Ag}^+ \parallel \text{Zn}^{++} \mid \text{Zn}$$

the e.m.f is negative ($E = -1.6$ volts). It can be immediately concluded that Ag will not dissolve to deposit zinc. The opposite arrangement will have positive e.m.f. and hence negative $\triangle G$. That is, zinc will spontaneously dissolve to deposit Ag.

The spontaneity of a reaction can be judged from the sign of the e.m.f. of the cell. The criteria are:

$\triangle G$	E	*Cell reaction*
$-$	$+$	spontaneous
0	0	equilibrium
$+$	$-$	non-spontaneous

18.2. Nernst Equation : EMF and Equilibrium Constant

From the reaction isotherm, the free energy change ($\triangle G$) for the cell reaction,

$$\triangle G = -RT\, ln\, K_a + RT\, \Sigma v\, ln\, a$$

where K_a is the eqm. constant and 'a'-terms denote activities.

If all the participants in the chemical process are in standard state, their activities would be unity, the standard free energy change ($\triangle G^\circ$) would be

$$\triangle G^\circ = -RT\, ln\, K_a \qquad \ldots (18.7)$$

Hence $$\triangle G = \triangle G^\circ + RT\, \Sigma v\, ln\, a \qquad \ldots (18.8)$$

From equation (18.4), if E be the e.m.f. of the cell in the given state and E° the standard e.m.f. of the cell, then

$$\triangle G = -nJE \text{ and } \triangle G^\circ = -nJE^\circ \qquad \ldots (18.9)$$

Substituting with equations (18.7 and 18.8),

(*i*) $$nJE^\circ = RT \ln K_a$$

or $$E^\circ = \frac{RT}{nJ} ln\, K_a = 2.303 \frac{RT}{nJ} \log K_a \qquad \ldots (18.10)$$

and (*ii*) $$nJE = nJE^\circ - RT\, \Sigma v\, ln\, a$$

or $$E = E^\circ - \frac{RT}{nJ} \Sigma v\, ln\, a,$$

$$= E^\circ - \frac{2.303\, RT}{nJ} \Sigma v \log a \qquad \ldots (18.11)$$

Also from eqns (18.10 and 18.11),

$$E = \frac{2.303\ RT}{n\mathcal{J}} \log K_a - \frac{2.303\ RT}{n\mathcal{J}} \Sigma \nu \log a \qquad \ldots (18.12)$$

In an approximate evaluation, K_a may be replaced by K_c and a-terms by concentrations assuming ideal behaviour.

The quantity $\frac{2.303\ RT}{\mathcal{J}}$ would occur very often in calculations of e.m.f. Its value for $T = 298°\text{K}$ is $\frac{2.303 \times 8.32 \times 298}{96500} = 0.0591$ ... (18.13)

$$\left.\begin{aligned} &\text{Hence at } 25°\text{C},\ E° = \frac{0.0591}{n} \log K_a \\ &E = E° - \frac{0.0591}{n} \Sigma \nu \log a \\ \text{and}\quad &E = \frac{0.0591}{n} \log K_a - \frac{0.0591}{n} \Sigma \nu \log a \end{aligned}\right\} \qquad \ldots (18.14)$$

These are the different forms of what is commonly known as '*Nernst equation*' for galvanic cells. It is evident that determination of e.m.f. would permit the evaluation of equilibrium constant and *vice versa*.

The validity of this relation was tested experimentally first by Knupffer (1898) who studied the cell,

$$\text{Tl(Hg}_x\text{)} \left| \begin{array}{l} \text{KCNS soln} \\ \text{satd. with TlCNS} \end{array} \right\| \begin{array}{l} \text{KCl soln} \\ \text{satd. with TlCl} \end{array} \Big| \ \text{Tl (Hg}_x\text{)}$$

Cell reaction : $\text{TlCl} + \text{KSCN} \rightleftharpoons \text{TlSCN} + \text{KCl}$

Since solid TlCl and TlSCN are present, their concentrations remain constant. From equation (18.12),

$$E = \frac{2.303\ RT}{\mathcal{J}} \log K_a - \frac{2.303\ RT}{\mathcal{J}} \log \frac{a_{\text{KCNS}}}{a_{\text{KCl}}} \quad \ldots (\text{since } n = 1)$$

$$\approx \frac{2.303\ RT}{\mathcal{J}} \log K_c - \frac{2.303\ RT}{\mathcal{J}} \log \frac{C_{\text{KCNS}}}{C_{\text{KCl}}}$$

At 20°C, the eqm. constant (K_c) of the process was found to be 1.24. The e.m.f. of the cell was then calculated to be 0.0051 and the e.m.f. experimentally observed was 0.0048 volts, (when the ratio $C_{\text{KCl}} : C_{\text{KSCN}} = 1.52$). The agreement is quite satisfactory.

A few illustrations of the application of Nernst equation are given here. (*i*) The standard e.m.f. of the Daniell cell is 1.1 volt at 25°C, and the reaction is

$$\text{Zn} + \text{Cu}^{++} \rightarrow \text{Cu} + \text{Zn}^{++}$$

$$\therefore \qquad K = \frac{a_{\text{Cu}} \times a_{\text{Zn}^{++}}}{a_{\text{Zn}} \times a_{\text{Cu}^{++}}} = \frac{a_{\text{Zn}^{++}}}{a_{\text{Cu}^{++}}} \quad (\text{since } a_{\text{Zn}} = a_{\text{Cu}} = 1)$$

Now $$E^\circ = \frac{RT}{n\mathfrak{F}} \ln K = \frac{0.0591}{2} \log K$$

i.e., $$1.1 = \frac{0.0591}{2} \log K, \qquad \text{whence } K = 1.7 \times 10^{37}$$

$\therefore$ At eqm. $a_{\text{Zn}^{++}} = 1.7 \times 10^{37}\, a_{\text{Cu}^{++}}$

In other words, the reaction practically proceeds to completion.

(*ii*) In a voltaic cell, the eqm. constant of the reaction,

$$Ag + Fe(ClO_4)_3 \rightleftharpoons AgClO_4 + Fe(ClO_4)_2$$

was found to be 0.50 at 25°C. The e.m.f. of the celll

$$Ag \mid Ag^+ \parallel Fe^{++} - Fe^{+++} \text{ (Pt), is then given by}$$

$$E^\circ = \frac{2.303\, RT}{\mathfrak{F}} \log (0.50) = 0.0591 \log (0.50) = -0.017 \text{ volt}$$

18.3. Single electrode potentials

A reversible cell consists of at least two electrodes—positive and negative. Each of these electrodes is known as a *half-cell* or *a single electrode*. The process occurring in the cell ultimately causes in a given electrode transfer of electrons from the electrode to the electrolyte or vice versa, resulting into a flow of current when the circuit is completed. The electrodes usually are formed by dipping a metal into an electrolyte and these may be of different types.

Type I. The simplest electrodes are formed when a metal or a non-metal is in contact with a solution containing its own ions. Thus, silver immersed in silver nitrate solution, copper in copper sulphate solution, etc. are examples of this type. Similarly, chlorine in contact with a chloride solution forms an electrode. The reactions occurring at the electrodes are:

$$Ag \rightleftharpoons Ag^+ + \epsilon, \qquad H \rightleftharpoons H^+ + \epsilon$$
$$Cu \rightleftharpoons Cu^{++} + 2\epsilon, \qquad Cl^- \rightleftharpoons Cl + \epsilon$$

In the case of non-metal electrodes, which are often non-conductors, an inert metal like Pt (coated with Pt-black) saturated with adsorbed non-metal serves the purpose of conduction. So, a hydrogen or chlorine electrode may be expressed as

$$(Pt),\ H_2,\ H^+\ ; \qquad (Pt\text{-}Ir),\ Cl_2,\ Cl^-$$

Type II. A metal with one of its sparingly soluble salt in contact with a solution having the same anion may also form a good electrode, *e.g.*;

$$Ag - AgCl(s),\ KCl \text{ solution};$$

$$Hg - HgCl(s),\ KCl \text{ solution}; \text{ etc.}$$

The reaction involved is as follows :

$$\begin{array}{ll} & 2Hg(s) \rightleftharpoons Hg_2^{++} + 2\epsilon \\ & \underline{Hg_2^{++} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s)} \\ \textit{i.e.,} & 2Hg(s) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2\epsilon \end{array}$$

It means that the chloride ion in the solution gives up its electron. This is virtually the same as the chlorine-gas electrode represented earlier as

$$Cl^- \rightleftharpoons Cl + \epsilon = \tfrac{1}{2}Cl_2 + \epsilon$$

Such electrodes are reversible with respect to the anion.

Type III. An inert metal, such as platinum, immersed in a solution containing a mixture of the oxidised and the reduced states of a system, constitutes an important type of an electrode.

Thus a Pt-wire dipped in a mixture of the solutions of Fe^{++} and Fe^{+++} salts, or Sn^{++} and Sn^{++++} salts etc. will serve as a single electrode. The reactions in such a case involve transfer of electrons between the oxidised and the reduced forms, *e.g.*,

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon$$

$$Sn^{++} \rightleftharpoons Sn^{++++} + 2\epsilon$$

$$Mn^{++} + 4H_2O \rightleftharpoons MnO_4^- + 8H^+ + 5\epsilon$$

$$\underset{\text{Hydroquinone}}{C_6H_4(OH)_2} \rightleftharpoons \underset{\text{Quinone}}{C_6H_4O_2} + 2H^+ + 2\epsilon, \text{ etc.}$$

These electrodes are often mentioned as 'oxidation-reduction' electrodes.

Oxidation, in modern terminology, means liberation or giving up of electrons. Thus ferrous ion is oxidised to ferric ion and zinc atom is oxidised to Zn^{++} ion, Cl^- ion is oxidised to chlorine atom,

$$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon$$

$$Zn \rightleftharpoons Zn^{++} + 2\epsilon$$

$$Cl^- \rightleftharpoons Cl + \epsilon, \text{ and so on.}$$

Reduction is the opposite process and it involves the acceptance or taking up of electrons, as Cu^{++} ions are reduced to Cu-atoms or Hg^{++} ions are reduced to Hg^+ ions by taking up electrons,

$$Cu^{++} + 2\epsilon \rightleftharpoons Cu$$

$$Hg^{++} + \epsilon \rightleftharpoons Hg^+; \text{ etc.}$$

Thus, Fe^{+++}, Zn^{++}, Cu^{++}, Cl etc. are the oxidised states called *oxidants*, and Fe^{++}, Zn, Cu, Cl^-, Hg^+ etc. are the reduced states, called *reductants*.

The three types of electrodes considered above are structurally different, but in every case, electrons are either liberated or taken up, the process being reversible. A reversible electrode therefore will involve an oxidant and a reductant. The process in the electrodes may be represented as

	Electrode Process	Oxidant	Reductant
Type I	$Zn \rightleftharpoons Zn^{++} + 2\epsilon$	Zn^{++}	Zn
Type II	$Hg + Cl^- \rightleftharpoons HgCl + \epsilon$	$HgCl$	Cl^-
Type III	$Fe^{++} \rightleftharpoons Fe^{+++} + \epsilon$	Fe^{+++}	Fe^{++}

Hence, in any electrode, the process involved may be expressed as :

$$\text{Reductant} \rightleftharpoons \text{Oxidant} + n\epsilon$$

When a galvanic cell yields electrical energy oxidation occurs at one electrode and reduction at the other. For example in the Daniell cell, while it gives current, zinc ionises at the negative electrode and copper ions are deposited at the positive. Hence, oxidation occurs at the zinc electrode and reduction at the copper electrode. This is generally true for all reversible cells.

Expression for Electrode Potentials : At each of the electrodes of the galvanic cell a potential exists which may be expressed as follows:

Consider a metal electrode in equilibrium with a solution of its ions,

$$M \mid M^{n+} \text{ ions} \ldots.$$

There are two phases — metal phase and the solution phase — and let these be denoted by suffixes I and II respectively. The metal ions are distributed in both the metal and the solution phase. Suppose their chemical potentials in the two phases are μ_{I} and μ_{II}. Let the electric potentials in the two phases be denoted by ψ_{I} and ψ_{II}. If the change at the electrode be $M \rightarrow M^{n+} + n\epsilon$, the potential should be termed oxidation potential of the electrode, $\mathscr{E}$. Obviously the oxidation potential of the electrode,

$$\mathscr{E} = \psi_{\text{II}} - \psi_{\text{I}}$$

If the valency of the metal ion be n, then the electrostatic energies per gm-mole of the metal ion would be $n\mathscr{F}\psi_{\text{I}}$ and $n\mathscr{F}\psi_{\text{II}}$ in the two phases.

At equilibrium the net molal Gibbs potential would be the same in the two phases, hence

$$\mu_{\text{I}} + n\mathscr{F}\psi_{\text{I}} = \mu_{\text{II}} + n\mathscr{F}\psi_{\text{II}}$$

The sum '$\mu + n\mathscr{F}\psi$' is also termed as *electro-chemical potential* of the system. Further,

$$\mu_{\text{I}} = z_{\text{I}}^{\circ} + RT \ln a_{\text{I}}, \qquad \mu_{\text{II}} = z_{\text{II}}^{\circ} + RT \ln a_{\text{II}}$$

where a_{I} and a_{II} are the activities of the metal ions in the metal and the solution phases. Substituting in the above relation,

$$n\mathcal{J}\psi_{\text{I}} + RT\ln a_{\text{I}} + z_{\text{I}}^{\circ} = n\mathcal{J}\psi_{\text{II}} + RT\ln a_{\text{II}} + z_{\text{II}}^{\circ}$$

or
$$\psi_{\text{II}}-\psi_{\text{I}} = \frac{z_{\text{I}}^{\circ}-z_{\text{I}}^{\circ}}{n\mathcal{J}} - \frac{RT}{n\mathcal{J}}\ln\frac{a_{\text{II}}}{a_{\text{I}}}$$

That is, $\mathscr{E} = \text{constant} - \dfrac{RT}{n\mathcal{J}}\ln\dfrac{a_{\text{II}}}{a_{\text{I}}}$

When a_{I} and a_{II} are unit activities, $\mathscr{E} = \mathscr{E}^{0} = \text{constant}$,

$$\therefore\ \mathscr{E} = \mathscr{E}^{0} - \frac{RT}{n\mathcal{J}}\ln\frac{a_{\text{II}}}{a_{\text{I}}} = \mathscr{E}^{0} - \frac{RT}{n\mathcal{J}}\ln\frac{a_{\text{ox}}}{a_{\text{red}}} \qquad \ldots (18.15)$$

Where a_{II} corresponds to the activity in the oxidised state and a_{1} to the reduced state. Thus for a Zinc-electrode,

$$\mathscr{E}_{\text{zn}} = \mathscr{E}_{\text{zn}}^{\circ} - \frac{RT}{2\mathcal{J}}\ln\frac{a_{\text{zn}^{++}}}{a_{\text{zn}}} \qquad \ldots (18.15a)$$

The e.m.f. of a voltaic cell is really the algebraic sum of the two single electrode potentials. (The junction potential is not considered at the moment).

An arbitrary standard is necessary for the quantitative expression of the single electrode potentials. The reversible hydrogen electrode prepared with H_2-gas at 1 atm (on Pt) in a solution of H^+-ions of unit activity is taken as the standard electrode and its potential has been accepted as zero (Fig 18*b*).

H_2-electrode : (Pt) H_2(1 atm) | H^+ (a = 1), $\mathscr{E}_{H_2} = 0$.

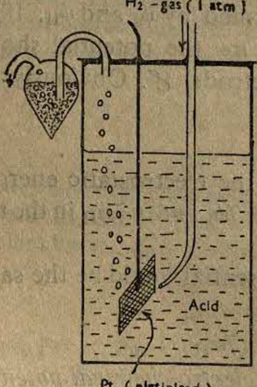


Fig. 18*b*
Hydrogen electrode

This is our standard electrode having zero potential. The potentials of other electrodes are compared to this standard. In determining the single electrode potentials the single electrode is coupled with a standard hydrogen electrode and the e.m.f. of the cell so formed is measured potentiometrically. For example, in determining the electrode potential of zinc, we construct a cell,

$$\text{Zn} \mid \text{Zn}^{++}{}_{(a_{\text{zn}^{++}})}\text{solution} \parallel \text{H}^{+}{}_{(a_{\text{H}^{+}}=1)} \mid H_2(gas)_{1\ \text{atm}}$$

and the e.m.f. of this cell E is measured.

Now, $E = \mathscr{E}_{Zn} + \mathscr{E}_{H_2} = \mathscr{E}_{Zn}$, since $\mathscr{E}_{H_2} = 0$, where $\mathscr{E}_{Zn}$ and $\mathscr{E}_{H_2}$ are the single electrode potentials. In this cell, it is known, that H_2-electrode is the positive and zinc electrode the negative of the cell, the current flowing from H_2 to Zn in the external circuit. The electrode reactions are,

Zn-electrode : $Zn \rightarrow Zn^{++} + 2\epsilon$
H_2-electrode : $2H^+ + 2\epsilon \rightarrow H_2$

The net chemical process, $Zn + 2H^+ = Zn^{++} + H_2$

The e.m.f. of this cell, then should be, from (18.14),

$$E = E^0 - \frac{RT}{n\mathcal{J}} \ln \frac{a_{Zn^{++}} . a_{H_2}}{a_{Zn} . a^2_{H^+}}$$

$$= E^0 - \frac{RT}{n\mathcal{J}} \ln \frac{a_{Zn^{++}}}{a_{Zn}} \qquad [\because a_{H^+} = a_{H_2} = 1]$$

This e.m.f. is really equal to the electrode potential of zinc only, the other electrode having zero potential. Hence,

$$\mathscr{E}_{Zn} = E^0 - \frac{RT}{n\mathcal{J}} \ln \frac{a_{Zn^{++}}}{a_{Zn}} = E^0 - \frac{RT}{n\mathcal{J}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

If we take the solution of Zn^{++} ions such that $a_{Zn^{++}} = 1$, and remembering $a_{Zn} = 1$, we have

$$\mathscr{E}^0_{Zn} = E^0$$

$$\therefore \qquad \mathscr{E}_{Zn} = \mathscr{E}^0_{Zn} - \frac{RT}{n\mathcal{J}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}} \qquad \ldots (18.16)$$

where $\mathscr{E}^0_{Zn}$ is the *normal electrode potential* of the electrode with the activities of oxidant and reductant as unity. (Sec eqn. 18.15*a*).

Regarding the sign of the electrode potential, there is some confusion in the literature. The widely accepted convention about the sign is that the potential of the single electrode in which the oxidation of the reduced state occurs should be considered as positive. To indicate the significance of the sign, the potential is better called '*the oxidation potential of the electrode*'. In the above cell, at the zinc electrode, zinc metal is oxidised to Zn^{++} ions, hence the potential of the zinc electrode would be positive.

But if we construct a cell with a zinc electrode and (say) a potassium electrode, $K \mid K^+ \parallel Zn^{++} \mid Zn$, then at the zinc-electrode, reduction of Zn^{++} ions into metallic zinc occurs.

$$2K + Zn^{++} \rightarrow Zn + 2K^{++}$$

The potential of the zinc electrode now will be the same oxidation potential of zinc with the sign reversed, *i.e.*, $[-\mathscr{E}_{Zn}]$. This will be true in every case. In other words, if during the passage of electricity reduction occurs at any electrode, its potential will be opposite to the oxidation-potential associated with that electrode.

Let us now consider some other single electrode potentials.

(A) To determine the electrode potential of copper, we shall take a cell,

$$(\text{Pt},)\ H_2\ (g) - \underset{(a_{H^+}\ =\ 1)}{H^+}\ \Big\|\ \underset{(a_{Cu^{++}})}{Cu^{++}} - Cu\ (\text{metal})$$

by coupling Cu-electrode with H_2-electrode. The cell is such that in the external circuit, the current passes from copper to hydrogen.

The electrode processes are

Cu − electrode, $Cu^{++} + 2\epsilon = Cu$ (reduction process)

H_2 − electrode, $H_2 = 2H^+ + 2\epsilon$ (oxidation process)

Net reaction of the cell : $H_2 + Cu^{++} = Cu + 2H^+$

$$\text{The e.m.f. of thecell, } E = E^0 - \frac{RT}{nJ}\ln\frac{a_{Cu}\times a^2_{H^+}}{a_{Cu^{++}}\times a_{H_2}}$$

$$= E^0 - \frac{RT}{nJ}\ln\frac{a_{Cu}}{a_{Cu^{++}}}$$

But $E = \mathscr{E}_{Cu} + \mathscr{E}^0_{H_2} = \mathscr{E}_{Cu}$ (since $E^0_{H_2} = 0$)

The e.m.f. of the cell is equivalent to the single electrode potential ($\mathscr{E}_{Cu}$) of the copper electrode in magnitude.

$$\text{Hence,}\qquad -E = -E^0 - \frac{RT}{nJ}\ln\frac{a_{Cu^{++}}}{a_{Cu}}$$

In the cell considered, the copper electrode involved a reduction process. So, $-E$ and $-E^0$ shall be oxidation potentials of copper. Since

$$\mathscr{E}_{Cu,Cu^{++}} = -\mathscr{E}_{Cu^{++},Cu}$$

$$\therefore\qquad -E = \mathscr{E}_{Cu} \text{ and } -E^0 = \mathscr{E}^0_{Cu}$$

Hence, in accordance with the convention of signs proposed,

$$\mathscr{E}_{Cu} = \mathscr{E}^0_{Cu} - \frac{RT}{nJ}\ln\frac{a_{Cu^{++}}}{a_{Cu}}$$

$$= \mathscr{E}^0_{Cu} - \frac{RT}{nJ}\ln\frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

This expression is the same as in eqn. (18.15).

(B) The electrode potential of an anion electrode, say that of chlorine may be obtained from the cell,

$$\begin{array}{r|l} \text{(Pt), } Cl_2\,(g) - Cl^- & H^+ - H_2\,(g), \text{(Pt)} \\ (a_{Cl^-}) & (a_{H^+}=1) \end{array}$$

the electrode processes are,

$$2Cl^- - 2\epsilon = Cl_2$$
$$2H^+ + 2\epsilon = H_2$$

Net reaction :

$$2H^+ + 2Cl^- = H_2 + Cl_2$$

The e.m.f.

$$E = E^0 - \frac{RT}{nJ} \ln \frac{a_{H_2}.a_{Cl_2}}{a^2_{H^+}a^2_{Cl^-}} = E^0 - \frac{RT}{nJ} \ln \frac{a_{Cl_2}}{a^2_{Cl^-}}$$

$$= E^0 - \frac{RT}{nJ} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

Since, $E = \mathscr{E}_{Cl_2}$ as the other electrode is a normal hydrogen electrode, we may write,

$$\mathscr{E}_{Cl_2} = \mathscr{E}^0{}_{Cl_2} - \frac{RT}{nJ} \ln \frac{a_{Cl_2}}{a^2{}_{Cl^-}} = \mathscr{E}^0{}_{Cl_2} - \frac{RT}{nF} \ln \frac{a_{\text{oxidan t}}}{a_{\text{reductant}}}$$

(C) In an oxidation-reduction electrode, the same method may be used. To determine the electrode potential of $Ce^{+++} - Ce^{++++}$ electrode, we may use the cell,

$$\begin{array}{l} \text{(Pt) } H_2\,(g),\ H^+ \quad \| \quad Ce^{+++},\ Ce^{++++} \text{ (Pt)} \\ \qquad (a_{H^+} = 1) \end{array}$$

The electrode processes are

$$Ce^{++++} + \epsilon = Ce^{+++} \text{ (reduction)}$$
$$H - \epsilon = H^+ \text{ (oxidation)}$$

Net reaction,

$$H + Ce^{++++} = H^+ + Ce^{+++}$$

The e.m.f. of the cell, in which $\mathscr{E}^0_H = 0$,

$$E = E^0 - \frac{RT}{nJ} \ln \frac{a_{H^+}.a_{Ce^{+++}}}{a_H.a_{Ce^{++++}}} = E^0 - \frac{RT}{nJ} \ln \frac{a_{Ce^{+++}}}{a_{Ce^{++++}}}$$

But this e.m.f. is equal to the reduction potential of cerous-ceric system. In terms of oxidation potential, the sign is reversed. So

$$-E = -E^0 + \frac{RT}{nJ} \ln \frac{a_{Ce^{+++}}}{a_{Ce^{++++}}}$$

or

$$\mathscr{E}_{\text{redox}} = \mathscr{E}^0{}_{\text{redox}} - \frac{RT}{nJ} \ln \frac{a_{Ce^{++++}}}{a_{Ce^{+++}}}$$

$$= \mathscr{E}^0{}_{\text{redox}} - \frac{RT}{nJ} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

It is thus seen that all different types of electrodes have their oxidation potentials expressed as,

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{n\mathfrak{J}} \ln \frac{a_{\text{oxidant}}}{a_{\text{reductant}}}$$

It is obvious that the magnitude of the electrode potential depends upon the activities of the ions in the electrolyte.

In every cell oxidation occurs at the negative electrode and reduction at the positive electrode. To compute the e.m.f. of the cell, take the sum of the oxidation potential of the negative electrode and the reduction potential of the positive electrode. It is to be remembered that the reduction potential of an electrode is the same as its oxidation potential with the sign changed.

The e.m.f. of the cell : $E = \mathcal{E}^{oxn}_{-ve} + \mathcal{E}^{red}_{+ve}$

$$= \mathcal{E}^{oxn}_{-ve} - \mathcal{E}^{oxn}_{+ve}$$

The normal emf of a cell is likewise the algebraic sum of the normal electrode potentials, say, for Daniell cell ; $E^0 = \mathcal{E}^0_{zn} - \mathcal{E}^0_{cu}$

To illustrate :

(*i*) Let us consider another cell, Cd | Cd^{++} ‖ Fe^{++}, Fe^{+++} (Pt) in which it is found that Cd is the negative electrode of the cell. The reaction is

$$\text{Cd} + 2\text{Fe}^{+++} \rightarrow \text{Cd}^{++} + 2\text{Fe}^{++}$$

The cell emf : $E = E^0 - \dfrac{RT}{n\mathfrak{J}} ln \dfrac{a_{\text{Cd}^{++}}.a^2_{\text{Fe}^{++}}}{a^2_{\text{Fe}^{+++}}}$,

(since $a_{\text{Cd}} = 1$) . . . (Y)

The oxidation potential of Cd-electrode is

$$\mathcal{E}_{\text{Cd}} = \mathcal{E}^0_{\text{Cd}} - \frac{RT}{n\mathfrak{J}} ln (a_{\text{Cd}^{++}}/a_{\text{Cd}}) = \mathcal{E}^0_{\text{Cd}} - \frac{RT}{n\mathfrak{J}} ln\ a_{\text{Cd}^{++}}$$

The oxidation potential of redox electrode (Fe^{++} – Fe^{+++}) is

$$\xi_{redox} = \left[\xi^0_{redox} - \frac{RT}{n\mathfrak{J}} ln \frac{a^2_{\text{Fe}^{+++}}}{a^2_{\text{Fe}^{++}}} \right]$$

Hence, $E = \xi_{\text{Cd}} + (-\xi_{redox})$

$$= \xi^0_{\text{Cd}} - \frac{RT}{n\mathfrak{J}} ln\ a_{\text{Cd}^{++}} - \xi^0_{redox} + \frac{RT}{n\mathfrak{J}} ln \frac{a^2_{\text{Fe}^{+++}}}{a^2_{\text{Fe}^{++}}}$$

$$= \left(\xi^0_{\text{Cd}} - \xi^0_{redox}\right) - \frac{RT}{n\mathfrak{J}} ln \frac{a_{\text{Cd}^{++}}.a^2_{\text{Fe}^{++}}}{a^2_{\text{Fe}^{+++}}}$$

$$= E^0 - \frac{RT}{n\mathfrak{J}} ln \frac{a_{\text{Cd}^{++}} a^2_{\text{Fe}^{++}}}{a^2_{\text{Fe}^{+++}}},$$

the same as in (Y) above.

(*ii*) Similarly, two oxidation-reduction electrodes may also constitute a cell. For example, in the cell

$$(\mathrm{Pt})\ \mathrm{Sn}^{2+},\ \mathrm{Sn}^{4+}\ \|\ \mathrm{Fe}^{2+},\ \mathrm{Fe}^{3+}\ (\mathrm{Pt})$$

the ferrous-ferric redox electrode serves as the cathode

$$\xi_{\mathrm{Fe}^{3+},\,\mathrm{Fe}^{2+}} = \xi^0_{\mathrm{Fe}^{2+},\,\mathrm{Fe}^{3+}} - \frac{RT}{J}\, ln\frac{a_{\mathrm{Fe}^{3+}}}{a_{\mathrm{Fe}^{2+}}}$$

Similarly, $\xi_{\mathrm{Sn}^{2+},\,\mathrm{Sn}^{4+}} = \xi^0_{\mathrm{Sn}^{2+},\,\mathrm{Sn}^{4+}} - \dfrac{RT}{2J}\, ln\dfrac{a_{\mathrm{Sn}^{4+}}}{a_{\mathrm{Sn}^{2+}}}$

$$\therefore\ \text{Cell emf, } E = \xi^0_{\mathrm{Sn}^{2+},\,\mathrm{Sn}^{4+}} - \xi^0_{\mathrm{Fe}^{2+},\,\mathrm{Fe}^{3+}} - \frac{RT}{2J}\frac{a_{\mathrm{Sn}^{4+}}.a^2_{\mathrm{Fe}^{2+}}}{a^2_{\mathrm{Fe}^{3+}}.a_{\mathrm{Sn}^{2+}}}$$

If after the numerical computation the e.m.f. of the cell is found to be negative, it is to be understood that the process is actually reverse of what is assumed and the current flows opposite way. The anodes and cathodes are to be interchanged.

$\mathscr{E}^0$, the standard electrode potential, is obtained when the activity of the ion in solution is unity. The standard electrode potential can be determined in two ways.

(*i*) The electrode potential is measured with a given solution as previously shown and the activity (or activity coefficient) of the ion is also measured separately. The methods of determination for the latter are given later. Then

$$\mathscr{E} = \mathscr{E}^0 - \frac{RT}{nJ}\ln a_+ = \mathscr{E}^0 - \frac{RT}{nJ}\ln m_+\gamma_+$$

where m_+ = molality of the ion.

$\mathscr{E}^0$ is known when $\mathscr{E}$ and γ_+ are separately determined.

(*ii*) The standard Gibbs potential change, $\triangle G^0$, is determined, for the reaction occurring in the cell, from measurement of equilibrium constant under standard conditions. Now

$$\triangle G^0 = -RT\ln K, \quad \text{also} \quad \triangle G^0 = -nJE^0$$

$$\text{Hence} \qquad E^0 = \frac{RT}{nJ}\ln K$$

Now, if the electrode potential of one of the half-cells be known, that of the other can be easily ascertained, for the total e.m.f. of the cell is the algebraic sum of the two electrode potentials,

$$E^0 = \mathscr{E}_1 + \mathscr{E}_2$$

To take an illustration, let us consider the reaction

$$Ag + Fe(ClO_4)_3 \rightleftharpoons AgClO_4 + Fe(ClO_4)_2$$

whose equilibrium constant at 25°C, after corrections with Debye equation, is 0.50 (Schumb et al).

The standard e.m.f. of the cell,

$$Ag-Ag^+ \,||\, Fe^{++}-Fe^{+++}(Pt)$$

$$E^0_{298} = \frac{RT}{\mathcal{J}} \ln K = 0.059 \log (0.50) = 0.017 \text{ volts.}$$

The electrode potential of Ag, $Ag^+ = -0.799$

$$E^0 = \mathscr{E}^0_{Ag} + \mathscr{E}^0_{Fe^{+++},\, Fe^{++}}$$

or $$-0.017 = -0.799 + E^0_{Fe^{+++},\, Fe^{++}}$$

or $$E^0_{Fe^{++},\, Fe^{+++}} = -0.783 \text{ volts}$$

The standard oxidation potentials of commonly used electrodes, are given in the Table appended below :

TABLE : STANDARD OXIDATION POTENTIALS OF SINGLE ELECTRODES AT 25°C
(Hydrogen Scale)

Electrode	Electrode Process	Potential
Li, Li^+	$Li \rightarrow Li^+ + \epsilon$	+3.024
Na, Na^+	$Na \rightarrow Na^+ + \epsilon$	+2.712
Zn, Zn^{++}	$Zn \rightarrow Zn^{++} + 2\epsilon$	+0.762
Fe, Fe^{++}	$Fe \rightarrow Fe^{++} + 2\epsilon$	+0.440
Cd, Cd^{++}	$Cd \rightarrow Cd^{++} + 2\epsilon$	+0.402
Ni, Ni^{++}	$Ni \rightarrow Ni^{++} + 2\epsilon$	+0.236
Sn, Sn^{++}	$Sn \rightarrow Sn^{++} + 2\epsilon$	+0.140
Pb, Pb^{++}	$Pb \rightarrow Pb^{++} + 2\epsilon$	+0.126
H_2, H^+	$\frac{1}{2}H_2 \rightarrow H^+ + \epsilon$	0.00
Cu, Cu^{++}	$Cu \rightarrow Cu^{++} + 2\epsilon$	−0.340
Hg, Hg_2^{++}	$2Hg \rightarrow Hg_2^{++} + 2\epsilon$	−0.799
Ag, Ag^+	$Ag \rightarrow Ag^+ + \epsilon$	−0.799
Cl_2, Cl^-	$Cl^- \rightarrow \frac{1}{2}Cl_2 + \epsilon$	−1.358
Br_2, Br^-	$Br^- \rightarrow \frac{1}{2}Br_2 + \epsilon$	−1.066
I_2, I^-	$I^- \rightarrow \frac{1}{2}I_2 + \epsilon$	−0.536
O_2, OH^-	$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2\epsilon$	−0.401
Ag, AgCl, Cl^-	$Ag + Cl^- \rightarrow AgCl + \epsilon$	−0.222
Hg, HgCl, Cl^-	$Hg + Cl^- \rightarrow HgCl + \epsilon$	−0.268
Pt, Sn^{++} Sn^{++++}	$Sn^{++} \rightarrow Sn^{++++} + 2\epsilon$	−0.150
Pt, Cu^+, Cu^{++}	$Cu^+ \rightarrow Cu^{++} + \epsilon$	−0.170
Pt, $FeCy_6^{-4}$, $FeCy_6^{3-}$	$FeCy_6^{4-} \rightarrow FeCy_6^{3-} + \epsilon$	−0.69
Pt, Fe^{++}, Fe^{+++}	$Fe^{++} \rightarrow Fe^{+++} + \epsilon$	−0.771
Pt, Hg_2^{++}, Hg^{++}	$Hg_2^{++} \rightarrow 2Hg^{++} + 2\epsilon$	−0.92
Pt, Ce^{+++}, Ce^{++++}	$Ce^{+++} \rightarrow Ce^{++++} + \epsilon$	−1.610

The knowledge of the electrode potentials is of considerable interest in analytical chemistry as well as in different electrochemical phenomena. Thus, Fe^{++}-Fe^{+++} has a lower oxidation potential than that of Sn^{++}-Sn^{++++} indicating stannous salts would reduce ferric salts, while Fe^{++} salts will not reduce stannic salts. Again, Ag-Ag^+ has a lower oxidation potential than that of Cu-Cu^{++}, *i.e.*, copper will displace Ag from $AgNO_3$ solution, but silver cannot displace copper from copper sulphate solution.

Another common application of the elecrode potentials is to evaluate the equilibrium constant of a reaction, where direct determination is difficult.

Example : The standard electrode potentials of copper and cadmium are −0.35 and 0.40 volts respectively at 25°C, what is the equilibrium constant of the reaction?

$$Cd + CuSO_4 \rightleftharpoons CdSO_4 + Cu,$$

The reaction ionically is : $Cd + Cu^{++} \rightleftharpoons Cu + Cd^{++}$

Hence $$K_a = \frac{a_{Cu} \times a_{Cd^{++}}}{a_{Cd} \times a_{Cu^{++}}} = \frac{a_{Cd^{++}}}{a_{Cu^{++}}}$$

The standard e.m.f. of the Cu − Cd cell, is $E^0 = 0.40 - (-0.35) = 0.75$

$$\therefore \qquad \frac{RT}{nJ} \ln K_a = E^0 = 0.75$$

At 25°C, $\frac{0.059}{2} \log K_a = 0.75$; or $K_a = 3.48 \times 10^2$

Other applications of electrode potentials, such as determination of activity etc., will be discussed later.

Problem (*i*) Compute the emf of the following cells:

$$(a)\quad (\text{Pt})\ \underset{(a=1)}{Fe^{++}} - \underset{(a=0.1)}{Fe^{+++}} \;\Big\|\; \underset{(a\,=\,0.001)}{Cl^-} \;\Big|\; AgCl(s) - Ag$$

$$(b)\quad Ag \;\Big|\; \underset{(a\,=\,0.01)}{Ag} \;\Big\|\; \underset{(a\,=\,0.1)}{Zn^{++}} \;\Big|\; Zn$$

(*a*) $$\xi_{Fe^{++}-Fe^{+++}} = \xi^0_{Fe^{++}-Fe^{+++}} - \frac{RT}{J}\, ln \frac{a_{Fe^{+++}}}{a_{Fe^{++}}}$$

$$= -0.771 - 0.059 \log \frac{0.1}{1.0} = -0.7120$$

$$\xi_{Ag-AgCl} = \xi^0_{Ag-AgCl} - \frac{RT}{J}\, ln \frac{1}{a_{Cl^-}}$$

$$= -0.223 - 0.059 \log \frac{1}{10^{-3}} = -0.3995$$

The standard ξ^0 values are taken from the table. Obviously Ag – AgCl electrode would be the anode and the spontaneous reaction is

$$Ag + Cl^- + Fe^{+++} \rightarrow AgCl + Fe^{++}$$

The e.m.f. of the cell is

$$E = \xi_{Ag-AgCl} - \xi_{Fe^{++}-Fe^{+++}}$$
$$= -0.3995 - (-0.7120) = 0.3125 \text{ volt}$$

(*b*)
$$\xi_{Ag} = \xi^0_{Ag} - 0.059 \log (.01) = -0.799 + 0.118$$
$$\xi_{Zn} = \xi^0_{Zn} - \frac{0.059}{2} \log (0.1) = 0.762 + 0.029$$

Hence Zn-electrode will act as anode. The e.m.f. of the cell is

$$E = E^0 - \frac{RT}{2J} \ln \frac{a_{Zn^{++}}}{a^2_{Ag^+}} = (\xi^0_{Zn} - \xi^0_{Ag}) - \frac{0.059}{2} \log \frac{0.1}{(0.01)^2}$$
$$= (0.762 + 0.799) - 0.089 = 1.472 \text{ volt}$$

Problem (*ii*) It is easy to evaluate the heat of reaction, entropy-change, etc. from a study of e.m.f. of cells at different temperatures. Take the cell,

$$Ag - AgBr(s) \mid KBr \text{ soln} \mid Hg_2Br_2(s) \mid Hg$$

The measured e.m.f.'s are 0.06839 at 25°C and 0.07048 at 30°C. Calculate, after stating the reaction involved, the values of the heat of reaction, free-energy change and entropy-change of the process.

The reaction may be represented as $2Ag + Hg_2Br_2 \rightleftharpoons 2AgBr + 2Hg$

$$\frac{dE}{dT} = \tfrac{1}{5}\,[0.07048 - 0.06839] = 4.2 \times 10^{-4}$$

Hence
$$\Delta S = nJ \frac{dE}{dT} = \frac{2 \times 96500 \times 4.2 \times 10^{-4}}{4.2} = 19.3 \text{ e.u.}$$

We have also, $\Delta G = -nJE = -\dfrac{2 \times 96500 \times 0.06839}{4.2} = -3143$ cal

The heat of reaction $\Delta H = \Delta G + T\Delta S = -3143 + 298 \times 19.3 = 2808$ cal

Problem (*iii*) The standard potentials for the electrodes $Hg \mid Hg_2^{++}$ and $Hg \mid Hg^{++}$ are -0.799 and -0.855 volts at 25°C. Calculate the equilibrium constant for the reaction : $Hg + Hg^{++} \rightleftharpoons Hg_2^{++}$.

Construct the cell, $Hg \mid Hg_2^{++} \parallel Hg^{++} \mid Hg$

The anodic process is $2Hg \rightarrow Hg_2^{++} + 2\epsilon$; $\xi^0_{Hg \mid Hg_2^{++}} = -0.799$

The cathodic process is $Hg^{++} + 2\epsilon \rightarrow Hg$; $\xi^0_{Hg \mid Hg^{++}} = -(-0.855)$

Cell reaction : $Hg + Hg^{++} \rightleftharpoons Hg_2^{++}$ $E^0 = +0.056$

Now
$$E^0 = \frac{RT}{2J} \ln \frac{a_{Hg_2}}{a_{Hg} \cdot a_{Hg^{++}}} = \frac{RT}{2J} \ln K$$

or
$$0.056 = \frac{0.059}{2} \log K, \qquad \text{whence } K = 79.07$$

18.4. Concentration cells

In this type of cells, the electrodes on the two sides are of the same material but they are dipped into solutions differing in the concentrations of the reversible ion ; such as,

$$\begin{array}{ll|l} (a) & \text{Ag}-\text{AgNO}_3\ sol^n\ (m_1) & \text{AgNO}_3\ sol^n\ (m_2)-\text{Ag} \\ & (a_{\text{Ag}^+} = a_1) & (a_{\text{Ag}^+} = a_2) \end{array}$$

$$\begin{array}{ll||l} (b) & \text{Zn}-\text{ZnSO}_4\ sol^n\ (m_1) & \text{ZnSO}_4\ sol^n\ (m_2)-\text{Zn} \\ & (a_{\text{Zn}^{++}} = a_1) & (a_{\text{Zn}^{++}} = a_2) \quad \text{etc.} \end{array}$$

The potentials of the two electrodes will not be the same as the concentrations (and hence the activities) of the reversible ions in the two solutions are not the same.

In drawing current from such a cell the two electrodes will operate in opposition. If we take the $AgNO_3$-concentration cell, at one electrode silver will be deposited while silver will be dissolved in the other and the process will continue until the activities in the two solutions become equal. Let us denote the activities of Ag^+ in the two solutions by a_1 and a_2, such that $a_2 > a_1$. In the natural process of attaining equilibrium, silver will be deposited on the electrode in the more concentrated solution, where, therefore, the process is one of reduction. If $\mathscr{E}_1$ and $\mathscr{E}_2$ denote the oxidation potentials of the electrodes, then the net e.m.f. of the cell will be

$$E = \mathscr{E}_1 - \mathscr{E}_2 = \left(\mathscr{E}_1^0 - \frac{RT}{nJ}\ln a_1\right) - \left(\mathscr{E}_2^0 - \frac{RT}{nJ}\ln a_2\right)$$

Since, the same metal is used in both electrodes, $\mathscr{E}_1^0 = \mathscr{E}_2^0$

Hence, $$E = \frac{RT}{nJ}\ln\frac{a_2}{a_1} \qquad \ldots (18.17)$$

Since $a_2 > a_1$, E is positive. Therefore, $\mathscr{E}_1 > \mathscr{E}_2$, *i.e.*, oxidation potential is greater in the electrode in dilute solution. The current will flow in the external circuit from the electrode dipped in more concentrated solution.

When the molal concentrations and activity coefficients are denoted by the symbols m and γ, then,

$$E = \frac{RT}{nJ}\ln\frac{m_2\gamma_2}{m_1\gamma_1} = \frac{RT}{nJ}\ln\frac{m_2}{m_1} + \frac{RT}{nJ}\ln\frac{\gamma_2}{\gamma_1}$$

The e.m.f. depends primarily on the concentration ratio m_2/m_1 of the two electrolytes, for which such cells are named concentration cells. Evidently, larger the ratio m_2/m_1, greater will be the e.m.f. of the cell. The concentration cells have often been used in the determination of the solubility of sparingly soluble salts, or the valency of an ion, etc.

18.5. Amalgam cells.

A galvanic cell may also be prepared by using amalgams as electrodes instead of pure metals. Two amalgams of different composition used in contact with a single electrolyte containing the reversible ion will form a galvanic cell, commonly called the amalgam cell ; such as

$$\begin{array}{l|c||r} \mathrm{Hg} - \overset{\psi_1}{\mathrm{Ag}(c_1)} & \mathrm{Ag}^+ \text{ in solution} & \overset{\psi_2}{\mathrm{Ag}\,(c_2)} - \mathrm{Hg} \\ \text{(activities)} : a_1 & a & a_2 \end{array}$$

Let us consider a silver-amalgam cell, in which the concentrations of silver in the two amalgams are c_1 and c_2 and the electrolyte is a silver-nitrate solution ; c_2 is greater than c_1.

Suppose μ_1 and μ_2 are the chemical potentials of silver ions in the two amalgams and let the electric potentials of the two electrodes be denoted by ψ_1 and ψ_2.

Then the net electro-chemical potentials of Ag^+ ions in the two electrodes would be given by

$$\begin{aligned} &\text{Electrode I} : && \mu_1 + nJ\psi_1 && = \mu_1{}^0 + nJ\psi_1 + RT \ln a_1 \\ &\text{Electrode II} : && \mu_2 + nJ\psi_2 && = \mu_2{}^0 + nJ\psi_2 + RT \ln a_2 \end{aligned}$$

The silver ions in both the amalgams are in equilibrium with the ions in electrolyte ; hence these two net potentials would be the same, each being equal to that of the Ag^+ ions in the electrolyte. Also reference standard $\mu_1{}^0 = \mu_2{}^0$. Hence,

$$\mu_1{}^0 + nJ\psi_1 + RT \ln a_1 = \mu_2{}^0 + nJ\psi_2 + RT \ln a_2$$

$$\therefore \quad \psi_2 - \psi_1 = \frac{RT}{nJ} \ln \frac{a_1}{a_2}$$

i.e., the e.m.f. of the cell, $E = \dfrac{RT}{nJ} \ln \dfrac{a_1}{a_2}$ . . . (18.18)

But $a_1 < a_2$, or E is negative ; *i.e.*, $\psi_1 > \psi_2$

This means that in the external circuit, the current will flow from the electrode, where the concentration of the amalgam is less.

18.6. Liquid Junction Potentials in Concentration Cells

When two solutions of different concentrations come in contact, a potential difference develops at the junction, called the *liquid junction potential*. The potential difference arises mainly due to the unequal rates of diffusion of the ions across the junction. In an electrolyte concentration cell, two different solutions of the same electrolyte are brought together and hence a liquid junction potential would arise.

Consider a HCl-concentration cell, as

$$(\text{Pt})\ \underset{\text{II}}{H_2-HCl}\ (a_2)\ \|\ HCl\ (a_1)-\underset{\text{I}}{H_2}\ (\text{Pt})$$

in which the solution of HCl in chamber II has a mean activity a_2 and that in chamber I a mean activity a_1, such that $a_1 > a_2$.

If liquid junction potential be eliminated, the e.m.f. of the cell would be the algebraic sum of the electrode potentials only, hence

$$E = \frac{RT}{\mathcal{J}}\, ln \frac{a_1}{a_2} \qquad \ldots (A)$$

But if the liquid junction potential (ξ_j) be not eliminated, the cell is,

$$(\text{Pt})\ \underset{\text{II}}{H_2 - HCl}\ (a_2)\ \vdots\ HCl\ \underset{\text{I}}{(a_1)}\ - H_2\ (\text{Pt})$$

the e.m.f. of the cell would be $E' = E + \xi_j$ $\qquad \ldots (B)$

The potential at the liquid junction cannot be measured directly. It is generally computed from the e.m.f. of the concentration cells.

Suppose, in the latter cell with transference, one faraday of electricity passes within the cell across the liquid junction. Remembering, the electrode in cell I is positive, there will be a transfer of t_+ gm-ions of H^+ from chamber II to chamber I, and a transfer of t_- gm-ions of Cl^- from chamber I to chamber II. This transfer-process may be represented as

$$t_+\ H^+_{II} + t_-\ Cl^-_{I} \rightarrow t_+\ H^+_{I} + t_-\ Cl^-_{II}$$

The free energy change of the transference-process is

$$\triangle G = -RT\, ln\, K_t + RT\, ln \frac{a^{t+}_{\underset{\text{I}}{H^+}} . a^{t-}_{\underset{\text{II}}{Cl^-}}}{a^{t+}_{\underset{\text{II}}{H^+}}\, a^{t-}_{\underset{\text{I}}{Cl^-}}}$$

The eqm. const. K_t can be evaluated, by putting $a_{\underset{\mathrm{I}}{\mathrm{H^+}}} = a_{\underset{\mathrm{II}}{\mathrm{H^+}}} = 1$ and $a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}} = a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}} = 1$ when $K_t = 1$, *i.e.*, $ln\ K_t = 0$. Hence,

$$\triangle G = RT\, ln \frac{a^{t+}_{\underset{\mathrm{I}}{\mathrm{H^+}}} . a^{t-}_{\underset{\mathrm{II}}{\mathrm{Cl^-}}}}{a^{t+}_{\underset{\mathrm{II}}{\mathrm{H^+}}} . a^{t-}_{\underset{\mathrm{I}}{\mathrm{Cl^-}}}} = RT \left[t_+\, ln \frac{a_{\underset{\mathrm{I}}{\mathrm{H^+}}}}{a_{\underset{\mathrm{II}}{\mathrm{H^+}}}} - t_-\, ln \frac{a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}}}{a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}}} \right]$$

$$= RT \left[t_+\, ln \frac{a_{\underset{\mathrm{I}}{\mathrm{H^+}}}}{a_{\underset{\mathrm{II}}{\mathrm{H^+}}}} - (1-t_+)\, ln \frac{a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}}}{a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}}} \right]$$

$$= RT \left[t_+\, ln \frac{a_{\underset{\mathrm{I}}{\mathrm{H^+}}} . a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}}}{a_{\underset{\mathrm{II}}{\mathrm{H^+}}} . a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}}} - ln \frac{a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}}}{a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}}} \right]$$

Since $a_{\underset{\mathrm{I}}{\mathrm{H^+}}} . a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}} = a_1^2$ and $a_{\underset{\mathrm{II}}{\mathrm{H^+}}} . a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}} = a_2^2$, where a_1, a_2 are the mean activities of the two HCl-solutions. Further, the ratio of the individual activities of an ion in the two solutions may be assumed to be equal to the ratio of the mean activities of the electrolytes, *i.e.*, $a_{\underset{\mathrm{I}}{\mathrm{Cl^-}}} / a_{\underset{\mathrm{II}}{\mathrm{Cl^-}}} = a_1/a_2$. So

$$\triangle G = RT \left[t_+\, ln \frac{a_1^2}{a_2^2} - ln \frac{a_1}{a_2} \right] = RT\,(2t_+ - 1)\, ln \frac{a_1}{a_2}$$

$$= RT(t_+ - t_-)\, ln \frac{a_1}{a_2} = -\frac{v-u}{v+u} RT\, ln \frac{a_1}{a_2}$$

where u, v are the mobilities of the H^+ and Cl^- ions respectively.

$$\left(t_+ = \frac{u}{u+v},\ t_- = \frac{v}{u+v} \right)$$

Now $\qquad \triangle G = -nJ\xi_j = -J\xi_j$

$$\therefore \qquad J\xi_j = \frac{v-u}{v+u} RT\, ln \frac{a_1}{a_2}$$

or $\qquad \xi_j = \dfrac{v-u}{v+u} \dfrac{RT}{J}\, ln \dfrac{a_1}{a_2} \qquad \ldots (18.19)$

The junction potential thus depends not only on the activities of the two solutions but also on the mobilities of the ions.

Substituting the values of E and ξ_j in equation (B) above, the e.m.f. of the cell with transference,

$$E' = \frac{RT}{\mathcal{J}} ln \frac{a_1}{a_2} + \frac{v-u}{v+u} \frac{RT}{\mathcal{J}} ln \frac{a_1}{a_2} = \frac{2v}{v+u} \frac{RT}{\mathcal{J}} ln \frac{a_1}{a_2}$$

$$= 2t_- . \frac{RT}{\mathcal{J}} ln \frac{a_1}{a_2} \qquad \ldots (18.20)$$

18.7. The Donnan Equilibrium

It has however been found that even careful measurements of osmotic pressure gave results for mol. wts. of macromolecules much lower than those obtained by other methods. The explanation came from Donnan (1911). In solution, say of a protein, there are giant ions having several units of charges which are counterbalanced by opposite charges of normal sized simple ions. When a protein solution is kept separated from an ordinary salt solution by a semipermeable membrane, it is expected the ordinary ions would only diffuse out, the giant macromolecular ion is indiffusible. But the small ions though diffusible through the membrane do not escape as the energy required to take these away from the field of the giant ion is quite high. The observed mol. wt. from osmometric experiment is thus a number average mol. wt. of the giant ion and the other ions dissociated from it. The Donnan's membrane effect would be understood from the following :

Suppose a semipermeable membrane separates a sodium chloride solution (conc. c_1) from a solution of NaP (conc. c_2), in which P^- is a non-diffusible macromolecular ion. Since P^- ions cannot diffuse but Cl^- ions can, the latter will pass from one side to the other. To maintain electrical neutrality, sodium ions will also diffuse. At equilibrium, an amount x of Na^+ and Cl^- ions would pass. The concentrations would be as follows, because of electrical neutrality in each chamber.

	I		II		
	Na^+	Cl^-	Na^+	P^-	Cl^-
Initially :	c_1	c_1	c_2	c_2	0
At eqm :	c_1-x	c_1-x	c_2+x	c_2	x

Since the chemical potential of NaCl will be the same at either side, $\mu_{\mathrm{NaCl_I}} = \mu_{\mathrm{NaCl_{II}}}$

Hence $\mu^0 + RT\, ln\, (a_{\mathrm{Na^+_I}} \cdot a_{\mathrm{Cl^-_I}}) = \mu^0 + RT\, ln\, (a_{\mathrm{Na^+_{II}}} \cdot a_{\mathrm{Cl^-_{II}}})$

i.e., $a_{\mathrm{Na^+I}} \cdot a_{\mathrm{Cl^-I}} = a_{\mathrm{Na^+II}} \cdot a_{\mathrm{Cl^-II}}$

Assuming ideal behaviour, $(c_1 - x)\ (c_1 - x) = (c_2 + x)x$,

or
$$\frac{x}{c_1} = \frac{c_1}{c_2 + 2c_1}$$

i.e., the fraction of NaCl diffused depends on c_2. If c_2 is large, the amount diffused would be smaller. It gives,

$$x = c_1^2/(c_2 + 2c_1). \qquad \ldots (Z)$$

The osmotic pressure of the solution is then,

$$\pi = RT\ \{(c_2 + x + x + c_2) - (c_1 - x) - (c_1 - x)\}$$

or
$$\pi = 2RT\,(c_2 - c_1 + 2x) = 2RTc_2\, \frac{(c_1 + c_2)}{(c_2 + 2c_1)}$$

(substituting x)

The measurements of osmotic pressure in such a condition, *i.e.*, 'swamping out' the Donnan effect by using high concentration of electrolytes, gave satisfactory results for mol. wts. of macromolecules.

Membrane Potential :

At equilibrium, the concentrations of Na^+ ions on the two sides of the membrane are different and so there will be a potential difference between the two compartments. Suppose the potential difference between the two sides, called *membrane potential*, is denoted by $\mathscr{E}_m$. If one faraday of electricity be passed across the potential difference, then as in a concentration cell (eqn. 18.17),

$$\mathscr{E}_m = \frac{RT}{\mathfrak{F}} \ln \frac{a_{\mathrm{Na^+(I)}}}{a_{\mathrm{Na^+(II)}}} \approx \frac{RT}{\mathfrak{F}} \ln \frac{C_{\mathrm{Na^+(I)}}}{C_{\mathrm{Na^+(II)}}}$$

$$= \frac{RT}{\mathfrak{F}} \ln \frac{C_1 - x}{C_2 + x} = \frac{RT}{\mathfrak{F}} \ln \frac{C_1}{C_1 + C_2}$$

(substituting Z)

Simplifying, $\mathscr{E}_m = \frac{RT}{\mathfrak{F}} \ln \left(1 - \frac{C_2}{C_1 + C_2}\right)$

$$\approx -\frac{RT}{\mathfrak{F}} \cdot \frac{C_2}{C_1 + C_2} \approx -\frac{RT}{\mathfrak{F}}\, \frac{C_2}{C_1},$$

in very dilute solutions, where C_2 is very small.

This is Donnan's equation for the membrane potential. The experiments of Sorensen and of Adair indicate the general validity of the Donnan relations. The later investigator showed the linearity of $\mathscr{E}_m$ against C_2/C_1 working with dilute haemoglobin solutions in water. These relations are valuable in making quantitative studies with colloid electrolytes, in contact with semi-permeable walls.

Problems

Use standard data from tables given in the book, where necessary.

1. Calculate the potentials of the following electrodes at 25°C :

(*a*) $Cu \mid Cu^{++} (a = 0.2)$

(*b*) $Pt \mid Fe^{++} - Fe^{+++}$

$(a = 0.1) \quad (a = 0.01)$

2. Compute the cell potentials of the following :

(*a*) $Pt \mid Fe^{2+} (a = 0.5), Fe^{3+} (a = 0.2) \parallel Cl^- (a = 0.001) \mid AgCl \mid Ag$

(*b*) $Pt \left| \begin{matrix} Tl^+ , & Tl^{+++} \\ (a = 0.5) & (a = 0.5) \end{matrix} \right\| \begin{matrix} Ce^{3+} , & Ce^{4+} \\ (a = 0.8) & (a = 0.2) \end{matrix} \Bigg| \; Pt$

3. The standard oxidation potentials of $Cu \mid Cu^{++}$ and $Cu \mid Cu^+$ are -0.337 and -0.530 volts. What is the equilibrium constant of the reaction,

$$2Cu^+ \rightleftharpoons Cu^{++} + Cu \; ?$$

4. The electrode potential of $Cu \mid Cu^{++}$ $(1M)$ is -0.62 volts. At what concentration will the electrode potential be zero?

5. The emf of the cell, $Tl \mid TlCl(s) \mid KCl\ (m = 0.1) \mid Hg_2Cl_2 \mid Hg$ is 0.73 volts and $dE/dT = 7.5 \times 10^{-4}$ volts/°K. Calculate ΔH and ΔG for the reaction.

6. The emf of the cell,
$Pt \mid Ce^{4+} (90\%),\ Ce^{3+} (10\%) \parallel$ normal calomel electrode, is 1.464 volts at 18°C. Calculate the eqm. constant for the reaction,

$$2Ce^{3+} + 2H^+ \rightleftharpoons 2Ce^{4+} + H_2$$

7. At 0°C, a calorimetric determination of ΔH for the reaction, $Zn + 2AgCl \rightleftharpoons ZnCl_2 + 2Ag$ yields the value $-$ 52.05 kcal. If the emf of the cell be 1.015 volts, what is the temperature coefficient of the cell? (C.U. 1979)

8. At 25°C, after addition of 110 ml of 0.1 N NaCl soln to 100 ml of 0.1 N $AgNO_3$ soln, the reduction potential of Ag-electrode placed in it is 0.36 volts. Assuming activities to be identical with concentration, calculate the solubility product of silver chloride. Given $\mathscr{E}^0_{Ag/Ag^+} = -0.799$ volts. (C.U. 1978)

9. At 25°C, the temp-coefficient of the e.m.f. of the cell,

$$Ag - AgCl - KCl\,(s) - Hg_2Cl_2 - Hg, \text{ is}$$

3.4×10^{-4} volts/degree. The cell reaction is

$$Ag\,(s) + \tfrac{1}{2}Hg_2Cl_2\,(s) = Hg(l) + AgCl\,(s).$$

The molar entropies at 25°C are $S_{Ag} = 10.2$, $S_{Hg} = 18.5$

and $S_{AgCl} = 23.0$ e.u.

Calculate $\triangle S°$ for the cell reaction and also the standard molar entropy of Hg_2Cl_2. **Ans.** $\triangle S° = 7.84$ e.u., $S_{Hg_2Cl_2} = 47.9$ e.u.

10. If the standard e.m.f. of the reversible cell in the preceding problem be 0.046 volts, what will be the Gibbs potential change of the reaction? **Ans.** 1049.7 *joules.*

11. In the cell,

$$Cd - CdSO_4(soln) \;\|\; Hg_2SO_4\,(soln) - Hg,$$

the e.m.f. at t°C, is $E_t = 0.6708 - 1.02 \times 10^{-4}\,(t - 25)$ volts. Calculate $\triangle G$ and $\triangle H$ at 45°C. **Ans.** $\triangle G = -30820$ cal, $\triangle H = -32283$ cal

12. For the cell, $Cd/CdCl_2\;(1m)\;AgCl/Ag$,

$$E_{298} = 0.675 \text{ volts and } dE/dT = -6.5 \times 10^{-4} \text{ volts/degree.}$$

Find $\triangle H_{298}$ and $\triangle S_{298}$ for the reaction $Cd + 2AgCl = Cd^{++} + 2Cl^- + 2Ag$.

13. Show that, for the cell,

$$Zn - Zn^{++}\,(a = 0.001) \;\left\|\; \begin{matrix} Fe^{++} & (a = 0.001), \\ Fe^{+++} & (a = 0.1)\;(Pt) \end{matrix}\right.$$

the e.m.f. would be 1.74 volts. (Consult standard tables).

14. The standard electrode potentials of $Cu/Cu^{++} = 0.345$ and $Hg/Hg^{++} = 0.799$ volts. Calculate the conc. of Hg^{++} ion at eqm, when metallic copper is placed in M/100 $HgCl_2$ solution.

15. For the cell, Cl_2 – molten $PbCl_2$ – Pb, the e.m.f. at t°C, $E_t = 1.30 - 6.8 \times 10^{-4}\;(t - 500)$. Caclulate the heat of formation of $PbCl_2$ at 500°C.

CHAPTER 19

IONIC EQUILIBRIUM
AND
THERMODYNAMIC PROPERTIES OF IONS

The solutions of electrolytes have positively and negatively charged ions. There is always an equilibrium between these ions and the undissociated molecules. Such equilibria are governed by thermodynamic criteria. A few of such ionic equilibria will be discussed here.

19.1. Solubility Product and Activity Product

When a saturated solution of a sparingly soluble salt, say AgCl, is in contact with the solid phase, the equilibrium is

$$AgCl(s) \rightleftharpoons AgCl\,(soln) \rightleftharpoons Ag^+ + Cl^-$$

At eqm, $\triangle G = 0$, hence, $\mu_{Ag^+} + \mu_{Cl^-} - \mu_{AgCl(s)} = \triangle G = 0$

$$\therefore \mu_{Ag^+} + \mu_{Cl^-} = \mu_{AgCl(s)} = \mu^{o}_{AgCl(s)} + RT\,ln\,a_{AgCl(s)} = \text{constant}$$

Hence $\mu^{o}_{Ag^+} + RT\,ln\,a_{Ag^+} + \mu^{o}_{Cl^-} + RT\,ln\,a_{Cl^-} = Z_1$ (constant)

Rewriting, $ln\ a_{Ag^+}.a_{Cl^-} = (Z_1 - \mu^{o}_{Ag^+} - \mu^{o}_{Cl^-})/RT$

$= Z_2$ (constant), at a constant temperature.

or $\quad a_{Ag^+}.a_{Cl^-} = e^{Z_2/RT} = L_a$ (constant) $\quad \ldots (19.1)$

L_a is called the *activity product* of the salt at a given temperature. It is the product of the activities of the ions in a saturated solution.

Expressing L_a with molar concentrations and activity coefficients,

$$L_a = C_{Ag^+}.{}_{Ag^+}.C_{Cl^-}.f_{Cl^-} = [C_{Ag^+}.C_{Cl^-}]f^2_{\pm} \quad \ldots (19.2)$$

In the saturated solutions of sparingly soluble salts, like AgCl, $BaSO_4$, HgS, etc in pure water, the concentrations of the ions will be very low ; hence $f_{\pm}$ is practically unity. Hence,

$$[C_{Ag^+}.C_{Cl^-}]f^2_{\pm} = C_{Ag^+}.C_{Cl^-} = L_s\,(\text{say}) \quad \ldots (19.3)$$

when L_s is called the *solubility product* of the salt.

Obviously, $\quad L_a = L_s.f^2_{\pm} \quad \ldots (19.4)$

This relation is valid for uni-univalent salts. For a salt like $Ca_3(PO_4)_2$ in saturated solution, $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{++} + 2PO_4^{---}$

$$L_a = a^3_{Ca^{++}} \times a^2_{PO_4^{---}} = [C^3_{Ca^{++}} \times C^2_{PO_4^{---}}]f^5_{\pm} = L_s.f^5_{\pm}$$

Generally speaking for a salt A_pB_q,

$$
\begin{aligned}
A_pB_q &= p\mathrm{A}^+ + q\mathrm{B}^- \\
\therefore \quad L_a &= C^p_{\mathrm{A}^+} f^p_+ \times C^q_{\mathrm{B}^-} . f^q_- \\
&= L_s \times f^\nu_\pm, \text{ where } \nu = p + q \qquad \ldots (19.5)
\end{aligned}
$$

For a given salt at a fixed temperature, the value of the thermodynamic activity product L_a is unchangeable. The solubility product L_s will be constant in ideal conditions only if $f_\pm$ is unity. In that case, since $f_\pm = 1$, $L_a = L_s$. For ordinary work dealing with very sparingly soluble salts, the solutions are so dilute that $f_\pm$ is regarded as unity, hence L_s is a constant.

If the solution contains other ions, then $f_\pm$ will change. The value of L_a remains constant, hence L_s shall also change.

Solubility Product and Solubility

Suppose S is the solubility of the sparingly soluble salt, AgCl, in pure water expressed in *gm-moles per litre*. Since the solution is very dilute even when saturated, the salt is assumed completely dissociated and the concentrations of the ions are

$$C_{\mathrm{Ag}^+} = S, \; C_{\mathrm{Cl}^-} = S$$

$$\therefore \text{ the solubility product, } L_s = S^2 \qquad \ldots (19.6)$$

So, an estimation of solubility enables one to determine the solubility product.

Similarly, for the solubility of $Mg(OH)_2$, we have

$$C_{\mathrm{Mg}^{++}} = S, \; C_{\mathrm{OH}^-} = 2S$$

$$\therefore \quad L_s = C_{\mathrm{Mg}^{++}} C^2_{\mathrm{OH}^-} = S \times (2S)^2 = 4S^3$$

In general, if S be the solubility of a salt A_pB_q in pure water, which is sparingly soluble, we have, $C_{\mathrm{A}^+} = pS$, $C_{\mathrm{B}^-} = qS$ assuming complete dissociation and $f_\pm = 1$, Then

$$L_s = C^p_{\mathrm{A}^+} \times C^q_{\mathrm{B}^-} = (pS)^p.(qS)^q = S^{p+q}.(p^pq^q)$$

$$
\left.
\begin{aligned}
\text{or} \quad L_s &= S^\nu.(p^p.q^q), \text{ where } \nu = p + q \\
\text{or} \quad S &= \left(\frac{L_s}{p^pq^q}\right)^{\frac{1}{\nu}}
\end{aligned}
\right\} \qquad \ldots (19.7)
$$

This is the relation between solubility and solubility product. This means that at a given temperature the solubility of a salt is constant.

Determination of activity product

(*a*) *To determine the activity product of silver chloride.*

Since $AgCl(s) \rightarrow Ag^+ + Cl^-\,;\quad K = a_{Ag^+} \times a_{Cl^-} = L_a$

Imagine two single electrodes as

$-$ *ve* electrode : $Ag(s) \rightarrow Ag^+ + \epsilon \qquad \xi^o_{Ag} = -0.7991$

and $+$ *ve* electrode : $AgCl(s) + \epsilon \rightarrow Ag(s) + Cl^- \qquad \xi^o_{Ag\text{-}AgCl} = -0.2223$

Hence,

$$E^\circ = \xi^o_{Ag} - \xi^o_{Ag\text{-}AgCl}$$

$$= -0.7991 + 0.2223 = -0.5768$$

Now

$$\log K = \frac{E^\circ}{0.059} \qquad \text{(at 25°C)}$$

i.e.,

$$\log L_a = \frac{E^\circ}{0.059} = -\frac{0.5768}{0.059}\text{, whence } L_a = 1.6 \times 10^{-10}$$

(*b*) It would be interesting to see how the solubility product can be evaluated thermodynamically from e.m.f. and ΔG-values.

At 25°C, the e.m.f. of the cell : $Zn \mid Zn^{++}(1\,m) \parallel H^+(1\,m)\text{–}H_2(Pt)$ (1 atm), is 0.761 volts.

It is known that the saturated H_2S-solution is 0.1 *M* and for the eqm,

$$H_2S \rightleftharpoons 2H^+ + S^{--}\,;\ \text{eqm. constant } K = 1.4 \times 10^{-20}$$

Further, the free energy of formation of H_2S and ZnS are

$$\Delta G^\circ_{H_2S(f)} = -8000 \text{ cal}, \qquad \Delta G^\circ_{ZnS(f)} = -43200 \text{ cal}$$

It is now possible to compute the solubility product by pursuing a succession of the following steps :

			Free energy change (ΔG°)
(*a*)	$H_2S_{(g)}$	$\rightleftharpoons H_2S\ aq.\ (0.1\ M)$	ΔG_1
(*b*)	$H_2S_{aq}\ (0.1\ M)$	$\rightleftharpoons H_2S_{aq}\ (1\ M)$	ΔG_2
(*c*)	$H_2(g) + S(s)$	$\rightleftharpoons H_2S(g)$	ΔG_3
(*d*)	$H_2S_{aq},\ (1\ M)$	$\rightleftharpoons 2H^+_{aq} + S^{--}_{aq}$	ΔG_4
(*e*)	$Zn(s) + 2H^+_{aq}$	$\rightleftharpoons Zn^{++}_{aq} + H_2(g)$	ΔG_5
(*f*)	$ZnS(s)$	$\rightleftharpoons Zn(s) + S(s)$	ΔG_6
Summing up	$ZnS(s)$	$\rightleftharpoons Zn^{++}_{aq} + S^{--}_{aq}$	ΔG°_s (say)

Now, the net free energy change, $\Delta G^\circ_S = \sum_1^6 \Delta G^\circ_n$, (when *P* and *T* are constant)

Now $\Delta G^\circ_1 = 0$, since $H_2S(g)$ is in eqm. with its solution.

$$\Delta G^\circ_2 = RT\,ln\,C_f/C_i \quad = 2\times2.303\times298\ \log 10 = 1372\text{ cal}$$

$$\Delta G^\circ_3 = \Delta G^\circ_{f(H_2S)} \quad = -8000\text{ cal}$$

$$\Delta G^\circ_4 = -RT\ ln\ K \quad = -2\times2.303\times298\log(1.4\times10^{-20}) = 27234\text{ cal}$$

$$\Delta G^\circ_5 = -nJE \quad = -2\times96540\ (0.761)\text{ joules} = 34996\text{ cal}$$

$$\Delta G^\circ_6 = -\Delta G^\circ_{ZnS(f)} \quad = 43200\text{ cal}$$

$$\therefore\ \Delta G^\circ s = \Sigma\Delta G^\circ_n = 0+1372-8000+27234-34996+43200 = 28810\text{ cal}$$

But $RT\,ln\,(L_s) = -\Delta G^\circ_s$, where L_s is the required solubility product

or $\quad 2\times298\times2.303\ \log L_s = -28810$

whence $\qquad L_s = 1\times10^{-21}$

19.2. Dissociation constants of Weak acids or bases

In solutions, weak electrolytes are only partially dissociated. There is always an equilibrium between the ions and the undissociated molecules of acids or bases. Such equilibria can be easily treated thermodynamically.

The dissociation of a weak acid or a weak base may be represented as

$$HA \rightleftharpoons H^+ + A^- \qquad\qquad BOH \rightleftharpoons B^+ + OH^-$$

In equilibrium, the chemical potential of the undissociated acid or base will be equal to the sum of the chemical potentials of the product ions.

$$\mu_{HA} = \mu_{H^+} + \mu_{A^-}\ ; \qquad \mu_{BOH} = \mu_{B^+} + \mu_{OH^-}$$

For a weak acid, then

$$\mu^\circ_{HA} + RT\ln a_{HA} = \mu^\circ_{H^+} + RT\ln a_{H^+} + \mu^\circ_{A^-} + RT\ln a_{A^-}$$

$$\text{or } RT\ln\frac{a_{H^+}\times a_{A^-}}{a_{HA}} = \mu^\circ_{HA} - \mu^\circ_{H^+} - \mu^\circ_{A^-} = k_1 \text{ (constant)}$$

$$\text{Hence, } \frac{a_{H^+}\times a_{A^-}}{a_{HA}} = k_a \text{ (constant)} \qquad \dots(19.8)$$

k_a is called the dissociation constant of the acid, HA. The activities may be expressed in molal or molar concentration with the corresponding activity coefficients. In e.m.f. measurements molality basis is usually employed, but in the study of degree of dissociation or of conductance, the molar concentrations are commonly used.

$$k_a = \frac{m_{H^+} \times m_{A^-}}{m_{HA}} \cdot \frac{\gamma_{H^+} \times \gamma_{A^-}}{\gamma_{HA}} \qquad \text{(molal)} \qquad \ldots (19.9)$$

$$k_a = \frac{C_{H^+} \times C_{A^-}}{C_{HA}} \cdot \frac{f_{H^+} \times f_{A^-}}{f_{HA}} \qquad \text{(molar)} \qquad \ldots (19.10)$$

For a weak base, we may have similar expressions for the dissociation constant of the base, *i.e.*,

$$k_b = \frac{a_{B^+} \times a_{OH^-}}{a_{BOH}} = \frac{C_{B^+} \times C_{OH^-}}{C_{BOH}} \cdot \frac{f_{B^+} \times f_{OH^-}}{f_{BOH}} \qquad \ldots (19.11)$$

If the molar concentration of the weak acid HA be C and if α be the degree of dissociation, then

$$C_{H^+} = \alpha C, \quad C_{A^-} = \alpha C, \quad C_{HA} = (1-\alpha)C$$

$$\therefore \quad k_a = \frac{\alpha C \times \alpha C}{(1-\alpha)C} \cdot \frac{f_{H^+} \times f_{A^-}}{f_{HA}} = \frac{\alpha^2 C}{1-\alpha} \cdot \frac{f_{H^+} \times f_{A^-}}{f_{HA}}$$

In dilute solutions, the activity coefficients be taken as unity,

$$k_a' = \frac{\alpha^2 C}{1-\alpha} \qquad \ldots (19.12)$$

which is the *Ostwald dilution law*. The Ostwald dissociation constant, k_a', will be a constant only at very low concentrations. At higher concentrations f-terms would differ from unity and k_a' would vary.

If λ_c and λ_∞ denote the equivalent conductances at concentration C and at infinite dilution, then $\alpha = \lambda_c/\lambda_\infty$.

Substituting, $$k_a' = \frac{\lambda_c^2 C}{\lambda_\infty(\lambda_\infty - \lambda_c)} \qquad \ldots (19.13)$$

In fact, very often the determination of the conductances is employed to find the value of the Ostwald's dissociation constant, k_a'.

If we anticipate that for uni-univalent ion the activity coefficient may be expressed as (Debye-Hückel),

$$\ln f_{H^+} = \ln f_{A^-} = -0.5056\, C_{H^+}^{\frac{1}{2}} = -0.5056\sqrt{\alpha C}$$

and the activity coefficient of the undissociated acid f_{HA} is taken as unity, then

$$\ln k_a = \ln k_a' - \ln \frac{f_{HA}}{f_{H^+} \times f_{A^-}}$$
$$= \ln k_a' - 1.011\sqrt{\alpha C}$$
$$\text{or} \quad \ln k_a' = 1.011\sqrt{\alpha C} + \ln k_a \qquad \ldots (19.14)$$

Both k_a' and αC are determined experimentally from conductivity values. The plot of k_a' against $\sqrt{\alpha C}$ yields the curve as shown in Fig. 19 *a*.

The linearity of the relation is easily seen at the lower ranges of concentration. The slope of the linear portion is the theoretically expected value of 1.01 The intercept gives the value of the true dissociation constant, k_a.

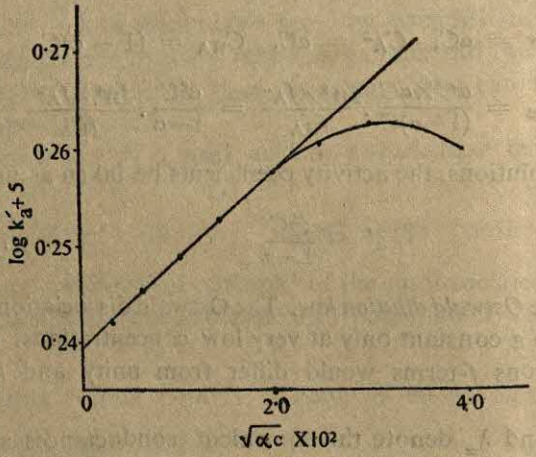


Fig 19.*a*. The plot of Ostwald's dissociation constant against $(\alpha C)^{\frac{1}{2}}$

The dissociation constant of an acid (or a base) can also be evaluated by determining the concentration of the H$^+$ ions in a solution containing the acid and a salt of the same. Let us consider a solution of acetic acid (conc. C) also containing sodium acetate (conc. C_1). Let the concentration of hydrogen ions be C_{H^+}, determined potentiometrically. Then

$$\text{conc. of acetic acid, HAC} = C - C_{H^+}$$
$$\text{conc. of acetate ion } (A_{C^-}) = C_1 + C_{H^+}$$

Hence, the dissociation constant of the acid,

$$K_a' = \frac{C_{H^+} \times C_{Ac^-}}{C_{HAc}} = \frac{C_{H^+}(C_1 + C_{H^+})}{C - C_{H^+}}$$

All the concentration terms on the rt-hand side being known, the value of K_a' is known.

19.3. Ionic Activity Product of Water

Water, a very weak electrolyte, dissociates to a very small extent

$$H_2O \rightleftharpoons H^+ + OH^-$$

In equilibrium, equating the chemical potentials of undissociated water with the products of its dissociation, we have

$$\mu_{H_2O} \rightleftharpoons \mu_{H^+} + \mu_{OH^-}$$

$$\text{or,}\quad RT \ln \frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}} = \mu^\circ_{H_2O} - \mu^\circ_{H^+} - \mu^\circ_{OH^-} = z \qquad \text{(constant)}$$

$$\therefore \qquad \frac{a_{H^+} \times a_{OH^-}}{a_{H_2O}} = a_{H^+} \times a_{OH^-} = k_w \text{ (constant)} \qquad \ldots (19.15)$$

since $a_{H_2O} = 1$, in pure water.

The constant k_w is called the *ionic activity product* of water. Replacing activities with concentrations and activity coefficients,

$$k_w = C_{H^+} \,.\, C_{OH^-} \,.\, f_{H^+} \,.\, f_{OH^-} = k_w' \, f_{H^+} \, f_{OH^-}$$

where k'_w is called the *ionic product* of water.

In pure water or in dilute solutions, the activity coefficients f_{H^+} and f_{OH^-} are almost unity, and so $k_w \approx k_w'$. That is, no appreciable error is involved in accepting ion product of water as its ionic activity product. In concentrared solutions k_w' varies considerably but k_w remains constant, at any given temperature.

At 25°C, the concentration of H+ ions in pure water is 1×10^{-7}. Since $C_{H^+} = C_{OH^-}$ in pure water, therefore

$$k_w' = C_{H^+} \,.\, C_{OH^-} = (1 \times 10^{-7})^2 = 1 \times 10^{-14}$$

The equation (19.15) really suggests that in an aqueous medium, the product of the concentrations of H^+ and OH^- should be constant. If we are dealing, not with pure water, but a dilute aqueous solution, this relation is still valid. In an acid solution, there is a preponderance of H^+ ions but nevertheless there would be some

OH^- ions, and the product of the two concentrations would be 1×10^{-14} at 25°C. Similarly in alkali solutions, there exist some H^+ ions. For example, in a $M/100$ HCl solution,

$$C_{OH^-} = \frac{C_{OH^-} \times C_{H^+}}{C_{H^+}} = \frac{k_w'}{C_{H^+}} = \frac{1 \times 10^{-14}}{1 \times 10^{-2}} = 1 \times 10^{-12}$$

The ion product of water can be determined accurately from measurement of e.m.f. of some suitable galvanic cells, such as

$$\begin{array}{c|c||c|c|c} (\mathrm{Pt})\ \mathrm{H_2} & \mathrm{KOH} & \mathrm{KCl} & \mathrm{AgCl}(s) & \mathrm{Ag} \\ (1\ \mathrm{atm}) & (m_1)) & (m_2) & & \end{array}$$

in which the cell reaction is, $AgCl(s) + \frac{1}{2}H_2 \rightarrow Ag(s) + H^+ + Cl^-$. So that its e.m.f.,

$$E = E^\circ - \frac{RT}{J} \ln \frac{a_{Ag(s)} . a_{H^+} . a_{Cl^-}}{a_{AgCl(s)} \times a_{H_2}^{\frac{1}{2}}}$$

$$= E^\circ - \frac{RT}{J} \ln a_{H^+}\, a_{Cl^-}, \text{ (since } a_{Ag} = a_{AgCl} = a_{H_2} = 1)$$

$$\therefore E = E^\circ - \frac{RT}{J} \ln \frac{k_w . a_{Cl^-}}{a_{OH^-}}$$

$$= E^\circ - \frac{RT}{J} \ln k_w - \frac{RT}{J} \ln \frac{m_{Cl^-}}{m_{OH^-}} - \frac{RT}{J} \ln \frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

$$\text{or } \left\{E - E^\circ + \frac{RT}{J} \ln \frac{m_{Cl^-}}{m_{OH^-}}\right\} = -\frac{RT}{J} \ln k_w - \frac{RT}{J} \ln \frac{\gamma_{Cl^-}}{\gamma_{OH^-}}$$

The value of E° is 0.2224 volts at 25°C.

The e.m.f. (E) of the cell is measured using various dilute solutions of KCl and KOH, *i.e.*, with different low values of m_{Cl^-} and m_{OH^-}. The left-hand side of this equation is then plotted against the ratio of the ionic strength of the KCl and KOH solutions used. The curve on extrapolation to infinite dilution of the solution, *i.e.*, zero ionic strength (where $\gamma_{Cl^-} = \gamma_{OH^-} =$ unity), gives the value of $-\frac{RT}{J} \ln k_w$.

The value of k_w was thus found to be 1.008×10^{-14} at 25°C.

19.4. Hydrolysis of salts

Water exhibits a hybrid character by behaving both as a weak acid and a weak base. As an acid it donates a proton (H^+) and as a base it accepts a proton,

$$\underset{\text{acid}}{H_2O} + \underset{\text{base}}{Ac^-} \rightarrow AcH + OH^-$$

$$\underset{\text{base}}{H_2O} + \underset{\text{acid}}{NH_4^+} \rightarrow NH_4OH + H^+$$

A salt of a strong acid and of a strong base, like NaCl, is not influenced by water. For neither the cation Na^+ has a tendency to combine with OH^- ions nor the anion Cl^- has a tendency to combine with OH^+ ions of the water.

But if we take a salt from a weak acid and a strong base, *e.g.*, sodium acetate (NaAc), a portion of the salt would be reacted upon by water and thus suffer hydrolysis.

$$NaAc + H_2O = HAc + NaOH$$

or, $$Na^+ + Ac^- + H_2O = HAc + Na^+ + OH^-$$

i.e., $$\underset{\text{base}}{Ac^-} + \underset{\text{acid}}{H_2O} = \underset{\text{acid}}{HAc} + \underset{\text{base}}{OH^-} \qquad \dots (A)$$

Concentrations $C(1-\beta)$ $\qquad \beta C \quad \beta C$

If C be the concentration of the salt in solution and β be the degree of hydrolysis, then

$$C_{Ac^-} = C(1-\beta), \qquad C_{HAc} = C_{OH^-} = \beta C$$

Now, for the reaction (A),

$$\mu^\circ_{Ac^-} + RT\ln a_{Ac^-} + \mu^\circ_{H_2O} + RT\ln a_{H_2O}$$
$$= \mu^\circ_{HAc} + RT\ln a_{HAc} + \mu^\circ_{OH^-} + RT\ln a_{OH^-}$$

or, $$RT\ln\frac{a_{OH^-}\times a_{HAc}}{a_{H_2O}\times a_{Ac^-}} = \Sigma\mu_i^\circ = z \text{ (constant)}$$

i.e., $$\frac{a_{OH^-}\times a_{HAc}}{a_{Ac^-}} = k_h \text{ (constant)}, \ [a_{H_2O} = 1] \qquad \dots (19.16)$$

k_h is called the hydrolytic constant.

Now, $$k_h = \frac{a_{OH^-}}{a_{Ac^-}}.a_{HAc} = k_w\frac{a_{HAc}}{a_{H^+}.a_{Ac^-}} = \frac{k_w}{k_a} \qquad \dots (19.17)$$

We have seen in the last section that k_w and k_a can be experimentally determined so k_h can be evaluated.

$$\text{Again, } k_h = \frac{a_{OH^-} \times a_{HAc}}{a_{Ac^-}} = \frac{C_{OH^-} \times C_{HAc}}{C_{Ac^-}} = \beta^2 C$$

(assuming $f_{OH^-}/f_{Ac^-} \approx 1$, and β being small)

$$\therefore \text{ degree of hydrolysis, } \beta = \sqrt{k_h/c} = \sqrt{k_w/(k_a.c)}$$

$$\text{And conc. of H}^+, \ C_{H^+} = k_w/C_{OH^-} = k_w/\beta C = \sqrt{\frac{k_w \times k_a}{C}}$$

Taking negative logarithms of both sides.

$$pH = \tfrac{1}{2} pk_w + \tfrac{1}{2} pk_a + \tfrac{1}{2} \log C$$

$$= 7.0 + \tfrac{1}{2} pk_a + \tfrac{1}{2} \log C\, ; \quad \left(\log_{10} \frac{1}{k_w} = pk_w\right) \qquad \ldots (19.18)$$

The solutions having *pH* below 7.0 are acidic and those having *pH* above 7.0 are alkaline. The acidity or alkalinity of a given salt solution can thus be easily known.

In the same way, similar expressions can be deduced for salts derived from strong acids and weak bases (*e.g.*, NH_4Cl) or for salts derived from weak acids and weak bases (*e.g.*, ammonium acetate, NH_4Ac).

In the case of

(*i*) Salts from a strong acid and a weak base

$$k_h = \frac{k_w}{k_b}\, ; \quad pH = 7.0 - \tfrac{1}{2} pk_b - \tfrac{1}{2} \log C$$

(*ii*) Salts from a weak acid and a weak base

$$k_h = \frac{k_w}{k_a . k_b}\, ; \quad pH = 7.0 - \tfrac{1}{2} pk_b + \tfrac{1}{2} pk_a$$

THERMODYNAMICS OF IONS

The transformation of atoms of elements into ions involve energy-changes, hence the thermodynamical properties such as enthalpy, entropy, free energy, etc. of the ions would be different from those of the atoms. The thermodynamic characteristics of ions would be taken up in this chapter.

19.5. Enthalpies of the formation of Ions

The heat of electrolytic reactions enable us to obtain an idea of the relative enthalpies of the formation of ions in dilute aqueous solutions. This has been discussed in Sec 3-5.

19.6. Free Energy of Ions in Solution

When an element is transformed into its ion, there would be a change in free energy. The free energy, G, of an element is taken as zero at the standard state, by convention. The change ($\triangle G$) in the formation of the ion is obviously the free energy or thermodynamic potential of the ion. An absolute value cannot be given to the free energy of an ion but it can be relatively expressed by accepting a standard value for a given ion. Usually, the free energy of the hydrogen ion at the standard state is accepted as zero ; $\overline{G^0}_{H^+} = 0$. That is, the standard free energy of formation of H^+-ion (*i.e.*, $H \rightarrow H^+$) is taken as zero.

(*a*) It is often convenient to determine the standard free energy of an ion from e.m.f. measurements. Let us take an illustration.

Consider the reaction when zinc is dissolved in dilute acid,

$$Zn + 2H^+ \rightarrow Zn^{++} + H_2$$

The free energy change in the process is given by,

$$\begin{aligned}\triangle G &= \mu_{Zn^{++}} + \mu_{H_2} - \mu_{Zn} - 2\mu_{H^+}\\ &= \mu^0_{Zn^{++}} + RT \ln a_{Zn^{++}} + \mu^0_{H_2} + RT \ln a_{H_2} - \mu^0_{Zn}\\ &\qquad - RT \ln a_{Zn} - 2\mu^0_{H^+} - 2RT \ln a_{H^+}\end{aligned}$$

When all the components are taken in the standard state with unit activities, and further because $\mu^0_{H_2} = \mu^0_{Zn} = \ldots = 0$, we have

$$\triangle G^0 = \mu^0_{Zn^{++}} - 2\mu^0_{H^+} = \overline{G}^0_{Zn^{++}} - 2\overline{G^0_{H}}^+ ,$$

as the chemical potentials (μ) are the partial molal free energies. Moreover, by convention, $\overline{G^0_{H^+}} = 0$,

$$\therefore \quad \triangle G^0 = \overline{G}^0{}_{Zn^{++}} \qquad \ldots (A_1)$$

If this reaction be carried out in a cell,

$$\underset{\text{Sol}^n}{Zn - ZnCl_2} \;\|\; \underset{\text{Sol}^n}{HCl - H_2}$$

with solutions having unit activity of ions, then

$$- \triangle G^0 = nJE^0 = nJ[\mathscr{E}^0_{Zn} - \mathscr{E}^0_{H_2}] = nJ\mathscr{E}^0_{Zn} \qquad \ldots (A_2)$$

E^0 = e.m.f. of the cell, $\mathscr{E}^0_{Zn}$ = electrode potential of zinc, and $\mathscr{E}^0_{H_2}$ = electrode potential of hydrogen = 0.

$$\therefore \ \triangle G^0 = \bar{G}^0_{Zn^{++}} = -nJ\mathscr{E}^0_{Zn} = -\frac{2 \times 96500}{4.2}\mathscr{E}^0_{Zn}$$

Similarly, for the formation of any positive ion, (M^{x+}),

$$M + xH^+ \rightarrow M^{x+} + \frac{x}{2}H_2$$

the standard free energy of the ion is

$$\bar{G}^0_{M^{x+}} = -xJ\mathscr{E}^0_M \qquad \ldots (19.19)$$

We may now consider the case of a negative ion, say the chloride ion. The change in the free energy ($\triangle G^0$) under standard states, for the reaction,

$$Cl^- + H^+ = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2$$

is given by, $\triangle G^0 = \tfrac{1}{2}\mu^0_{Cl_2} - \mu^0_{H^+} - \mu^0_{Cl^-} + \tfrac{1}{2}\mu^0_{H_2}$

By convention, $\mu^0_{Cl_2} = \mu^0_{H^+} = \mu^0_{H_2} = \ldots = 0$;

$$\therefore \quad \triangle G^0 = -\mu^0_{Cl^-} = -\bar{G}^0_{Cl^-}$$

For the cell, $H_2 - HCl\,(aq) - Cl_2$, under standard states,

$$\triangle G^0 = -nJE^0 = -nJ[\mathscr{E}_{Cl_2} - \mathscr{E}^0_{H_2}] = -nJ\mathscr{E}^0_{Cl_2}$$

$$\therefore \quad \bar{G}^0_{Cl^-} = nJ\mathscr{E}^0_{Cl_2}$$

For any negative ion B^{x-}, $\quad B + \frac{x}{2}H_2 = B^{x-} + xH^+$

The standard free energy of the ion,

$$B^{x-} = +xJ\mathscr{E}^0_B \qquad \ldots (19.20)$$

(*b*) It is evident that if the standard electrode potentials $(M \rightarrow M^+)$ or $(B \rightarrow B^-)$ can be directly measured the standard free nergy can be easily obtained. But when a reversible electrode between the element and its ion cannot be made, the free energy of the ion is to be determined indirectly.

Let us attempt to find out the thermodynamic potential of Sn^{++++} ion. The $\mathscr{E}^0_{Sn,\,Sn^{++++}}$ cannot be directly measured.

But we know, for the reaction

$$Sn \rightarrow Sn^{++} + 2\epsilon\ ; \quad \mathscr{E}^0_{Sn,\,Sn^{++}} = +0.140 \qquad \ldots (A_1)$$

and, $Sn^{++} \rightarrow Sn^{++++} + 2\epsilon; \mathscr{E}^0_{Sn^{++},Sn^{++++}} = -0.150 \ldots (A_2)$

The standard free energy changes are,

$$\Delta G^0{}_1 = -2\mathcal{J}(0.140)\ ;\ \text{and}\ \Delta G^0{}_2 = -2\mathcal{J}(-0.15)$$

Adding the two processes, $Sn \rightarrow Sn^{++++} + 4\epsilon$

$$\Delta G^0 = (-0.28\mathcal{J} + 0.30\mathcal{J}) = 0.02\mathcal{J}$$

$$= 0.02 \times \frac{96500}{4.2}\ \text{cal} = +459\ \text{cal}$$

The standard free energy per gm. ion of stannic ion is 459 cal.

Problem : Using standard electrode potentials calculate the free energy of ferric ions.

From the table, we have

(1) $Fe \rightarrow Fe^{++} + 2\epsilon$ $\qquad \mathscr{E}^\circ_{Fe-Fe^{++}} = +0.440$ (I)

(2) $Fe^{++} \rightarrow Fe^{+++} + \epsilon$ $\qquad \mathscr{E}^\circ_{Fe^{++}-Fe^{+++}} = -0.770$ (II)

$$Fe \rightarrow Fe^{+++} + 3\epsilon$$

The ΔG-values of the processes together,

$$\Delta G = -(2\mathcal{J}\mathscr{E}^\circ_{I} + \mathcal{J}\mathscr{E}^\circ_{II})$$

$$= -2\mathcal{J}(0.44) - \mathcal{J}(-0.77) = -0.11\mathcal{J} = -2528\ \text{cal}$$

∴ The thermodynamic potential of ferric ion = − 2528 cal. per gm. ion

In the table appended below are listed the standard free energy values of some of the common ions in aqueous solution.

TABLE : THE STANDARD FREE ENERGIES OF IONS IN KCAL. AT 25°C

Ion	$\overline{G}^\circ$	Ion	$\overline{G}^\circ$
Na^+	− 62.59	Cl^-	− 31.33
K^+	− 67.43	Br^-	− 24.58
Ag^+	+ 18.44	I^-	− 12.33
Ca^{++}	−132.70	NO_3^-	− 26.25
Mg^{++}	−107.78	OH^-	− 37.60
Zn^{++}	− 35.18	S^{--}	−128.42
Fe^{++}	− 20.30	SO_4^{--}	−176.10
Al^{+++}	−115.50	CO_3^{--}	−126.40
Fe^{+++}	− 2.53	PO_4^{---}	−241.00
Cu^{++}	+ 15.91	H^+	0.00

19.7. Standard entropies of ions

In a saturated solution the dissociation of a sparingly soluble salt, B_xA_y occurs as,

$$B_xA_y = xB^+ + yA^-$$

The entropy-change ΔS^0 due to dissolution is the difference of the entropies of the resultant ions and the entropy of the solid salt.

i.e.,
$$\Delta S^0 = \Sigma S^0_{\text{ions}} - S^0_{\text{solid}} \qquad \ldots (19.21)$$

But
$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \qquad \ldots (19.22)$$

A knowledge of the two quantities ΔH^0 and ΔG^0 would then enable us to determine ΔS^0. We may proceed to ascertain the values of ΔH^0 and ΔG^0 in the following way. In a saturated solution under equilibrium, the chemical potential of the solid (μ_s) will be equal to the sum of the chemical potentials of the ions ;

$$\mu_s = x\mu_+ + y\mu_-$$

or
$$\mu_s^\circ + RT\ln a_s = x\mu_+^\circ + y\mu_-^\circ + RT\ln a_+^x a_-^y$$

Now $x + y$ = number of ions produced = ν (say)

and
$$a_s = 1, \qquad a_+^x . a_-^y = a_\pm^\nu$$

Further, putting m = molality of the solute in solution and γ = mean activity coefficient of the solute,

$$x\mu_+^\circ + y\mu_-^\circ - \mu_s^\circ = - RT\ln a_+^x a_-^y$$

or
$$- \Delta G^0 = - \nu RT\ln a_\pm = - \nu RT\ln (m\gamma)_{\text{sat}} \qquad \ldots (19.23)$$

Using Helmholtz relation, we have

$$\Delta H^0 = \nu RT^2 \left[\frac{\partial \ln (m\gamma)}{\partial T}\right]_P \qquad \ldots (19.24)$$

where ΔH^0 is the increase in the heat content due to the dissolution of the salt in saturated solution. When the molality of the solution is known and the activity coefficient is determined separately (say, by applying Debye-Hückel Law), then both ΔH^0 and ΔG^0 would be known.

In the case of a sparingly soluble salt, the solution would be extremely dilute and the salt would be completely ionised. In such conditions γ may be taken as unity and the molality m may be replaced by solubility (s) of the salt.

That is,
$$\left.\begin{aligned} -\triangle G^0 &= \nu RT \ln s \\ \triangle H^0 &= \nu\, RT^2 \left(\frac{d \ln s}{dT}\right)_P \end{aligned}\right\} \quad \ldots (19.25)$$

So, in salts like silver chloride, the solubility measurements at different temperatures would enable us to calculate $\triangle G^0$ and $\triangle H^0$.

We have also an alternative method of measuring $\triangle H^0$. Suppose the heat-contents of the ions in standard states in dilute solution be denoted by H^0_+ and H°_- and let the heat-content of the solid be H_s. Then, increase in the heat-content due to the dissolution of the salt

$$\triangle H^0 = xH^0_+ + yH^0_- - H_s = \overline{H}_2{}^0 - H_s$$

where $\overline{H}_2{}^0$ is partial motal heat-content of the solute at infinite dilution. Thus $\triangle H^0$ is the heat of solution of the salt at infinite dilution. $\triangle H^0$ may thus be obtained from calorimetric measurement of the heat of precipitation of the salt from the dilute but saturated solution with the sign changed.

From equation (19.22 and 19.23)

$$\triangle S^0 = \frac{\triangle H^0 + \nu\, RT \ln (m\gamma)}{T}$$

$$i.e., \quad \Sigma\, S^0_{\text{ions}} - S_s = \frac{\triangle H^0}{T} + \nu R \ln m + \nu R \ln \gamma \quad \ldots (19.26)$$

For a sparingly soluble salt, m = solubility s, and $\gamma = 1$,

$$\therefore \quad \Sigma S^0_{\text{ions}} = S_s + \frac{\triangle H^0}{T} + \nu R \ln s \quad \ldots (19.27)$$

In the case of silver chloride,

$$S^0{}_{\text{Ag}^+} + S^0{}_{\text{Cl}^-} = S_{\text{AgCl}} + \frac{\triangle H^0}{T} + \nu R \ln C_{\text{Ag}^+}$$

The entropy of the solid state (S_s) can be determined from the heat capacity measurement by the application of the third law. The equation (19.27) thus enables us to calculate the sum of the ion entropies. The absolute value of the entropy of an ion cannot be fixed. Only the relative value can be obtained with reference to a standard value given to a definite ion. By convention, the entropy of the H$^+$ ion ($S^\circ{}_{\text{H}^+}$) has been fixed as zero.

Now if we carry out the dissolution of the metal B in dilute acid, as

$$B + xH^+ = B^{x+} + \frac{x}{2} H_2,$$

the standard thermodynamic potential of B^{x+} will be given by

$$G^\circ_{B^+} = -xJ\mathscr{E}^\circ_{B^+} = -x\frac{96500}{4.2}\mathscr{E}^\circ_{B^+}$$

and the entropy-change of the process would be,

$$\triangle S^\circ = S^\circ_{B^+} + \frac{x}{2} S^\circ_{B_2} - S^\circ_B - xS^\circ_{H^+}$$

$$(\because \; S^\circ_{H^+} = 0) \quad = S^\circ_{B^+} + \frac{x}{2} S^\circ_{H_2} - S^\circ_B \qquad \ldots (19.28)$$

$$\therefore \; \frac{\triangle H^0 - \triangle G^0}{T} = S^\circ_{B^+} + \frac{x}{2} S^\circ_{H_2} - S^\circ_B$$

or

$$S^\circ_{B^+} = S^\circ_B - \frac{x}{2} S^\circ_{H_2} + \frac{\triangle H^0}{T} + \frac{xJ\mathscr{E}^\circ_{B^+}}{T}$$

The last two terms on the right-side are experimentally determined and the standard entropies of the elements (B and H_2) can be taken from the Table. The entropy of the metal ion (B^+) is thus known.

Equation (19.27) gives us, $\Sigma S^\circ_{\text{ions}}$ *i.e.*, $(S^\circ_{B^+} + S^\circ_{A^-})$

Since $\Sigma S^\circ_{\text{ions}}$ and $S^\circ_{B^+}$ are known, $S^\circ_{A^-}$ is also evaluated.

The entropy of the reversible ion $S^\circ_{B^+}$ can also be found out if its standard electrode potential at more than one temperature be known. From Gibbs-Helmholtz relation we know,

$$\triangle S^0 = xJ\left(\frac{\partial \mathscr{E}^\circ_{B^+}}{\partial T}\right)$$

Applying equation (19.28),

$$S_{B^+} = S^\circ_B - \frac{x}{2} S^\circ_{H_2} - xJ\left(\frac{\partial \mathscr{E}^\circ_{B^+}}{\partial T}\right)$$

The standard entropies of some of the common ions are tabulated below:

TABLE: STANDARD MOLAR ENTROPIES OF IONS AT 25°C IN CAL/ PER GM-ION-DEGREE

Ion	S^0	Ion	S^0
Na^+	14.0	OH^-	− 2.5
K^+	24.2	Cl^-	13.5
Ag^+	17.5	Br^-	19.7
NH_4^+	26.5	I^-	25.3
Mg^{++}	−31.6	CO_3^{--}	−13.0
Ca^{++}	−11.4	SO_4^{--}	4.4
Cu^{++}	−26.5	S^{--}	− 5.5
Zn^{++}	−25.7	NO_3^-	35.0
Cd^{++}	−15.6	ClO_3^-	39.4
Hg_2^{++}	17.7	PO_4^{---}	−45.0
Sn^{++}	− 4.9	NO_2^-	29.9
Pb^{++}	3.9	MnO_4^-	46.7
Fe^{++}	−25.9	CN^-	25.0
Fe^{+++}	−61.0		
Al^{+++}	−76.0	H^+	− 0.0

Examples(i).Entropy of a cation : (*a*) The temperature coefficient of the standard Ag – Ag^+ electrode potential is 0.967×10^{-3} volt/degree. Determine the entropy of the Ag^+ ion.

$$Ag + H^+ = Ag^+ + \tfrac{1}{2}H_2$$

$$\therefore \qquad \Delta S^0 = S^0_{Ag} + \tfrac{1}{2}S^0_{H_2} - S^0_{Ag} - S^0_{H^+}$$

$$\text{or} \qquad S^0_{Ag^+} = S^0_{Ag} - \tfrac{1}{2}S^0_{H_2} + \Delta S^0$$

$$\text{But} \qquad \Delta S^0 = xJ\frac{\partial \mathscr{E}^0}{\partial T} \text{ and } S^0_{Ag} = 10.2;\; S^0_{H_2} = 31.2 \text{ (from tables)}$$

$$\therefore \qquad S^0_{Ag^+} = 10.2 - 15.6 + \frac{96500}{4.2}(0.967 \times 10^{-3}) = 16.8 \text{ e.u./gm ion.}$$

(*b*) The heat of solution per gm atom of cadmium in dilute acid is − 17500 calories at 25°C. The entropies of Cd metal and H_2 are 12.3 and 31.2 respectively and $\mathscr{E}^\circ_{Cd.Cd^{++}} = 0.402$ volts.

Calculate the standard entropy of the cadmium ion.

$$\mathrm{Cd} + 2\mathrm{H}^{+} = \mathrm{Cd}^{++} + \mathrm{H}_2$$

$$\Delta S^{0} = S^{0}_{\mathrm{Cd}^{++}} + S^{0}_{\mathrm{H}_2} - S^{0}_{\mathrm{Cd}} - 2S^{0}_{\mathrm{H}^{+}}$$

$$\therefore \quad S^{0}_{\mathrm{Cd}^{++}} = S^{0}_{\mathrm{Cd}} - S^{0}_{\mathrm{H}_2} + \Delta S^{0} = S^{0}_{\mathrm{Cd}} - S^{0}_{\mathrm{H}_2} + \frac{\Delta H^{0} - \Delta G^{0}}{T}$$

$$= S^{0}_{\mathrm{Cd}} - S^{0}_{\mathrm{H}_2} + \frac{\Delta H^{0}}{T} + \frac{2\mathcal{F}\mathcal{E}^{0}_{\mathrm{Cd}}}{T}$$

$$= 12.3 - 31.2 - \frac{17500}{298} + \frac{2 \times 96500}{4.2 \times 298}\,(0.402) = 12.45 \text{ e.u./gm ion}$$

Example (ii). Entropy of an anion: The solubility of AgCl in pure water at 25°C is 1.32×10^{-5} and the mean activity coefficient is 0.9985. The heat of the solution of the salt is 15740 cal. The entropies of solid AgCl and of Ag^{+} ion are 22.97 and 17.5 respectively. Calculate the standard entropy of the chloride ion. We know :

$$\Sigma S^{0}_{\mathrm{ions}} = S^{0}_{\mathrm{AgCl}} + \frac{\Delta H^{0}}{T} + 2R \ln (m\gamma)$$

or

$$S^{0}_{\mathrm{Cl}^{-}} = S^{0}_{\mathrm{AgCl}} + \frac{\Delta H^{0}}{T} + 2 \times 2 \times 2.303 \log (m\gamma) - S^{0}_{\mathrm{Ag}^{+}}$$

$$= 22.97 + \frac{15740}{298} + 9.2 \log (1.32 \times 0.9985 \times 10^{-5}) - 17.5$$

$$= 14.08 \text{ e.u. per gm. ion}$$

The determination of ionic entropies and ionic thermodynamic potentials is very useful in calculating the electrode potentials which cannot be directly measured.

Example (iii). Electrode potential of Aluminium. The heat of solution of aluminium in dilute acid is − 126300 calories and the standard entropies of Aluminium, Hydrogen and Al^{+++} ion are 6.75, 31.2 and − 76.0 respectively, calculate the standard electrode potential of aluminium.

It is given

$$\mathrm{Al} + 3\mathrm{H}^{+} = \mathrm{Al}^{+++} + \tfrac{3}{2}\mathrm{H}_2\,; \qquad \Delta H^{0} = -126300 \text{ cal}$$

The entropy-change of the process,

$$\Delta S^{0} = S^{0}_{\mathrm{Al}^{+++}} + \tfrac{3}{2} S^{0}_{\mathrm{H}_2} - S^{0}_{\mathrm{Al}} - 3S^{0}_{\mathrm{H}^{+}}$$

$$= -76.0 + \tfrac{3}{2} \times 31.2 - 6.75 - 3 \times 0 = -35.96 \text{ e.u.}$$

Then,

$$\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$$

$$= -126300 - 298(-35.96) = -115610 \text{ cal}$$

But

$$\Delta G^{0} = \bar{G}_{\mathrm{Al}^{+++}} + \tfrac{3}{2}\bar{G}^{0}_{\mathrm{H}_2} - \bar{G}^{0}_{\mathrm{Al}} - 3\bar{G}^{0}_{\mathrm{H}^{+}}$$

The last three terms are separately zero,

$$\therefore \quad \bar{G}^{0}_{Al^{+++}} = \Delta G^{0} = -115610$$

$$\therefore \quad -3\mathscr{J}\mathscr{E}^{0}_{Al} = -115610$$

or

$$\mathscr{E}^{0}_{Al} = \frac{-115610 \times 4.2}{-3 \times 96500} = 1.67 \text{ volts}$$

Example (*iv*). *Electrode potential of the fluorine electrode* : In order to determine the electrode potential of an anion electrode, usually the heat of formation of a salt of the anion in solution at infinite dilution is measured. This data together with the knowledge of the entropies of the ions and elements constituting the salt enables us to find out the electrode potential.

Given the entropies : $S^{0}_{Na} = 12.3, \quad S^{0}_{F_2} = 47.0$

$S^{0}_{Na^+} = 14.0, \quad S^{0}_{F^-} = -2.3$

and the electrode potential $\mathscr{E}^{0}_{Na,Na^+} = 2.712$. The heat of formation of sodium fluoride in solution at infinite dilution is − 136 K cal.

That is,

$$Na + \tfrac{1}{2}F_2 = Na^+ + F^-(aq); \quad \Delta H^0 = -136000 \text{ cal}$$

$$G^{0}_{Na^+} = -n\mathscr{J}\mathscr{E}^{0}_{Na} = -1 \times \frac{96500}{4.2} \times 2.712 = -62566 \text{ cal}$$

The entropy-change,

$$\Delta S^0 = S^{0}_{Na^+} + S^{0}_{F^-} - S^{0}_{Na} - \tfrac{1}{2}S^{0}_{F_2}$$

$$= 14.0 - 2.3 - 12.3 - 23.5 = -24.1$$

Now $\quad \Delta G^0 = \Delta H^0 - T\Delta S^0 = -136000 - (298)\,(-24.1) = -128819$ cal

But

$$\Delta G^0 = \bar{G}^{0}_{Na^+} + \bar{G}^{0}_{F^-} - \bar{G}^{0}_{Na} - \tfrac{1}{2}\bar{G}^{0}_{F_2}$$

$$= \bar{G}^{0}_{Na^+} + \bar{G}^{0}_{F^-} - 0 - 0$$

$$\therefore \quad \bar{G}^{0}_{F^-} = \Delta G^0 - \bar{G}^{0}_{Na^+} = -128819 + 62566 = -66253 \text{ cal}$$

$$\therefore \quad \mathscr{E}^{0}_{F} = \frac{\bar{G}^{0}_{F^-}}{n\mathscr{J}} = -\frac{66253}{1 \times 23070} = -2.87 \text{ volts}$$

Example (*v*). *Calculation of activity product* : The standard thermodynamic potentials of $PbSO_4$, Pb^{++} and SO_4^{--} are −195, −5.8 and −176 kcal respectively. Calculate the activity product of lead sulphate at 25°C.

When $PbSO_4$ is dissolved in an infinitely dilute solution,

$$PbSO_4 \rightleftharpoons Pb^{++} + SO_4^{--}$$

the change in thermodynamic potential of the process is

$$\Delta G^0 = \bar{G}^{0}_{Pb^{++}} + \bar{G}^{0}_{SO_4^{--}} - G^{0}_{PbSO_4} = 13.2 \text{ kcal}$$

Again $\Delta G^0 = -RT\ln(L_a)$; (L_a is the activity product)

or $$\text{og}\,(L_a) = -\frac{13200}{2\times298\times2.303}$$

or $$L_a = 1.09\times10^{-11}$$

Problems

1. For $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$; $\Delta H^0 = 15650$ cal
Given $S^0_{AgCl} = 22.97$, $S^0_{Ag^+} = 17.67$, and $S^0_{Cl^-} = 13.17$ e.u.
Calculate the solubility product of AgCl at 25°C. [Ans. 1.8×10^{-10}]

2. The solubility product of PbI_2 is 7.5×10^{-9} at 15°C and 1.4×10^{-8} at 25°C. Show that the molar heat of solution of PbI_2 = 10.600 cal. Calculate the solubility of PbI_2 at 35°C.

3. Calculate the solubility of TlBr at 25°C separately from the data given below :

(*i*)	TlBr	Tl^+	Br^-
ΔG^0_f	−39.7	−7.8	−24.6 kcal

(*ii*) For the cell, $Tl - TlBr(s) \mid Br^- \parallel Tl^+ \mid Tl(s)$
the emf is $E^\circ = 0.322$ volt. [Ans : (*i*) 4.5×10^{-6} (*ii*) 3.6×10^{-6}]

4. At 10°C, the ionic product of water is 0.314×10^{-14} and at 34°C it is 2.16×10^{-14}. Calculate the heat of formation of water from H^+ and OH^- ions.

5. Calculatethe percentage hydrolysis of sodium acetate in 0.1 N solution at 25°C. [$k_{\text{acetic acid}} = 1.8\times10^{-5}$; $k_w = 1.2\times10^{-14}$]

6. Calculate the ionic product of water from the emf of the following cell at 25°C :

$$(Pt) - H_2\,(1\ \text{atm}) \mid KOH\ (0.01\ m) \parallel KCl\ (0.01\ m) \mid AgCl(s)\text{-}Ag.$$
$$E^0 = 1.0503\ \text{volts.}$$

7. Calculate :

(*a*) the standard potential of Ag-Ag^+ electrode if the thermodynamic potential of Ag^+ is 18.44,

(*b*) the entropy of the Zn^{++} ion, if the temp-coefficient of the electrode potential of zinc is -1.02×10^{-4} and the entropy of solid zinc is 9.96 e.u.

(*c*) the ionic product of water at 25°C, if the standard thermodynamic potentials of OH^- and of $H_2O\,(l)$ be − 37.6 and − 56.7 kcal respectively.

8. The following data for $BaSO_4$ at 25°C are given,

$S^0_{BaSO_4} = 31.5$ e.u. $\qquad \Delta H_{\text{Soln}} = 5970$ cal

$S^0_{Ba^{++}} = 2.3$ e.u. $\qquad$ Solubility $= 9.6\times10^{-8}$ molal

what will be the entropy of SO_4^{--} ion?

CHAPTER 20

SOME OTHER INTERESTING APPLICATION OF THERMODYNAMICS

I. MAGNETO-CALORIC EFFECT : ADIABATIC DEMAGNETISATION

20.1. Types of magnetism

The electrons of an atom are responsible for its magnetism. The rotation of the electrons in closed orbits is virtually equivalent to a circular current and thus every rotating electron behaves like a magnetic shell possessing a magnetic moment.

(*a*) When the individual moments of the surrounding electrons in an atom cancel each other and there is no net moment, the atom becomes *diamagnetic*. If a magnetic field be applied to this, the orbits are altered such that the acquired moment is proportional to the field. The diamagnetism is independent of temperature.

(*b*) In many cases the electronic orbits are such that there is a small magnetic moment associated with the atoms. When a magnetic field is applied the atoms would tend to line up the moments in a definite direction. With low field strength the effect is proportional to the field but it tends to reach a constant value at high fields. This is *paramagnetism*. It depends on temperature and decreases with rise in temperature.

(*c*) When the net magnetic moment is large, the atoms arrange and align themselves in a pattern of ordered groups. A small field even would induce a large magnetisation in such cases. This is called *ferro-magnetism*.

A paramagnetic substance has the chance of acquiring ferromagnetic property if the temperature be lowered. The temperature of transition from the paramagnetic to the ferromagnetic state is called the *Curie-point* (or Curie temperature) of a substance. Thus iron has a Curie point (1043°K) and Gadolinium sulphate (nearly 1°K).

The co-ordinates used in dealing with magnetic properties may be mentioned.

(*i*) The *magnetising field* (also called magnetic intensity), denoted by $\mathscr{H}$, is expressed in dynes per pole called Oersteds. An Oersted is the measure of the magnetic intensity when a unit pole placed in the field is acted upon by a force of one dyne.

(*ii*) The *intensity of Magnetisation*, $\mathscr{I}$, is defined as the magnetic moment per unit volume. It is expressed in pole-strength per unit area. The magnetisation of a gm-mole of a substance is denoted by $\mathscr{M}$, such that $\mathscr{M} = \mathscr{I} \times V$.

(*iii*) The magnetic susceptibility, κ, is the ratio of the magnetisation $\mathscr{I}$ to the magnetic field, $\mathscr{H}$,

$$\kappa = \frac{\mathscr{I}}{\mathscr{H}}$$

For many paramagnetic substances the susceptibility varies inversely as the absolute temperature, i.e.,

$$\kappa = \frac{C}{T}, \text{ where } C \text{ is a constant.}$$

In other words, $\mathscr{M} = \kappa V \mathscr{H} = C . \frac{\mathscr{H}}{T} V \qquad \ldots (20.1)$

This is the well-known *Curie's equation* and C is called the *curie constant.*

(*iv*) The work of magnetisation may be represented by $-\mathscr{H} d\mathscr{M}$ the product of the field and the increase in magnetisation. The negative sign is due to work being done on the system.

20.2. Thermodynamics of paramagnetic substances

Taking into consideration the magnetic work in a given system of a paramagnetic substance, we have from the First Law,

$$dQ = TdS = dU + PdV - \mathscr{H} d\mathscr{M}$$

When only the magnetisation or the magnetic field changes, the pressure and the volume of the system practically remain unaltered, hence

$$TdS = dU - \mathscr{H} d\mathscr{M}$$

That is, for such processes, T, $\mathscr{H}$ and $\mathscr{M}$ may be regarded as the variable parameters of the system. So, we can write, the enthalpy,

$$H = U + PV - \mathscr{H}\mathscr{M}$$

the Gibbs potential, $G = U + PV - TS - \mathscr{H}\mathscr{M}$

Their differentials should be (P and V constant),

$$dH = dU - \mathscr{H}d\mathscr{M} - \mathscr{M}d\mathscr{H} = TdS - \mathscr{M}d\mathscr{H} \qquad \ldots (a)$$

$$dG = dU - TdS - SdT - \mathscr{H}d\mathscr{M} - \mathscr{M}d\mathscr{H} = -SdT - \mathscr{M}d\mathscr{H} \qquad \ldots (b)$$

From (a) $\left(\frac{\partial H}{\partial S}\right)_{\mathscr{H}} = T$; $\quad \left(\frac{\partial H}{\partial \mathscr{H}}\right)_S = -\mathscr{M}$

or $\quad \frac{\partial^2 H}{\partial S \partial \mathscr{H}} = \left(\frac{\partial T}{\partial \mathscr{H}}\right)_S$; $\frac{\partial^2 H}{\partial \mathscr{H} \partial S} = -\left(\frac{\partial \mathscr{M}}{\partial S}\right)_{\mathscr{H}}$

Hence, $\quad \left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\left(\frac{\partial \mathscr{M}}{\partial S}\right)_{\mathscr{H}} \qquad \ldots (c)$

From (b), $\quad \left(\frac{\partial G}{\partial T}\right)_{\mathscr{H}} = -S$; and $\left(\frac{\partial G}{\partial \mathscr{H}}\right)_T = -\mathscr{M}$

$$\frac{\partial^2 G}{\partial T \partial \mathscr{H}} = -\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T ; \frac{\partial^2 G}{\partial \mathscr{H} \partial T} = -\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}}$$

Hence, $\quad \left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} \qquad \ldots (d)$

Equations (c), (d) are really Maxwell's relations substituting P by $-\mathscr{H}$ and V by $\mathscr{M}$

We may further define $C_{\mathscr{H}}$ as the heat-capacity of a mole of the paramagnetic substance under a constant field, $\mathscr{H}$. So,

$$C_{\mathscr{H}} = \left(\frac{\partial q}{\partial T}\right)_{\mathscr{H}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathscr{H}} \qquad \ldots (e)$$

Now from equation (c), we obtain, on integration, under adiabatic conditions,

$$(\triangle T)_S = T_f - T_i = -\int_{\mathscr{H}_i}^{\mathscr{H}_f} \left(\frac{\partial \mathscr{M}}{\partial S}\right)_{\mathscr{H}} d\mathscr{H}$$

$$= -\int_{\mathscr{H}_i}^{\mathscr{H}_f} \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} \left(\frac{\partial T}{\partial S}\right)_{\mathscr{H}} d\mathscr{H}$$

$$= -\int_{\mathscr{H}_i}^{\mathscr{H}_f} \frac{T}{C_{\mathscr{H}}} \left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} d\mathscr{H} \qquad \text{(from } e\text{)}$$

or, $$T_f - T_i = -\frac{T}{C_{\mathscr{H}}}\int_{\mathscr{H}_i}^{\mathscr{H}_f}\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} d\mathscr{H} \qquad \dots (f)$$

Since variation of temperature would be small $C_{\mathscr{H}}$ may be considered as constant.

This relation gives us the variation of temperature with magnetisation. The phenomenon is often called *magneto-caloric effect.*

From Curie Law, $\mathscr{M} = C\frac{\mathscr{H}V}{T}$, or, $\left(\frac{\partial \mathscr{M}}{\partial T}\right)_{\mathscr{H}} = -\frac{C\mathscr{H}V}{T^2}$

Rewriting equation (*f*),

$$T_f - T_i = -\frac{T}{C_{\mathscr{H}}}\int_{\mathscr{H}_i}^{\mathscr{H}_f}\left(-\frac{CV}{T^2}\right)\mathscr{H} d\mathscr{H} = \frac{CV}{TC_{\mathscr{H}}}\int_{\mathscr{H}_i}^{\mathscr{H}_f}\mathscr{H} d\mathscr{H}$$

It is evident that under adiabatic conditions, if there is an increase in the field, the temperature would rise, or when adiabatic demagnetisation occurs temperature would fall. The physical significance of this may be understood in the following way. The entropy of a paramagnetic solid may be regarded as partly thermal and partly magnetic. When this is placed in a magnetic field, the atomic magnetic dipoles arrange themselvs in an order and hence entropy decreases. Now if the system is thermally insulated (*i.e.*, *S* remains constant) and the field is removed, the demagnetisation takes place, the atomic magnetic dipoles distributed at random cause an increase in magnetic entropy. The total entropy however remains constant. The thermal entropy, therefore, must decrease. This thermal entropy is measused by the thermal motion and hence when thermal entropy decreases the temperature must also fall. Adiabatic demagnetisation thus leads to cooling. This would apply only when magnetic entropy is appreciable compared to the thermal entropy. It is realised only at very low temperatures.

When the field is reduced to zero from its initial value $\mathscr{H}_i$, then

$$\Delta T = T_f - T_i = -\frac{CV}{T_i C_{\mathscr{H}}}\cdot\frac{\mathscr{H}_i^2}{2} \qquad \dots (g)$$

indicating drop in temperature.

Since $C_{\mathscr{H}}$ becomes very small near absolute zero, hence the drop in temperature would be appreciale only at very low temperatures, provided the paramagnetic behaviour exists at that temperature. At ordinary temperature, even with $\mathscr{H} = 10^4$ oersteds, $\triangle T$ is of the order of 0.001°. But at low temperatures of a few degrees absolute, $C_{\mathscr{H}}$ falls very rapidly and so $\triangle T$ becomes appreciable. In fact, Giauque and Debye independently showed that extermely low temperatures in the vicinity of absolute zero may be attained by the adiabatic demagnatisation of suitable paramagnetic substances at as low a temperature as possible. Onnes pointed out that Gadolinium sulphate, $Gd_2(SO_4)_3$, $8H_2O$ satisfies the conditions required. Giauque and Macdougall carried out the first adiabatic demagnetisation of Gadolinium sulphate and reached a low temperature of 0.53°K. Later, experiments were carried out by de-Haas, Simon & Kurti, and others and a temperature as low as 0.0014°K has been attained. In these experiments, different salts like Iron-ammonium-alum, chromium-potas-alum, ceric-ethyl-sulphate, copper-potassium-sulphate, etc. have been used. Salts having smaller interactions between the magnetic moments of their ions would be suittable for the purpose. An outline of the experiment may be given.

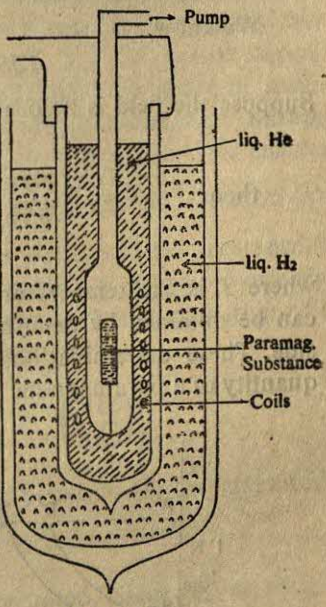


Fig. 20*a*

The paramagnetic salt in the form of an ellipsoid or a sphere of compressed powder is placed in a narrow container (Fig. 20*a*) in an atmosphere of Helium gas. The container is surrounded by liquid Helium cooled to nearly 1°K. The whole thing is enclosed in a narrow vacuum jacket and immersed in low temperature thermostat of liquid Hydrogen. The pumps and manometers are attached to the system for necessary evacuation and pressure measurements. Fine coils, primary and secondary, are placed round the container to measure magnetic susceptibility when desired. The entire arrangement is kept between the poles of an electromagnet, which can be switched off and wheeled away readily for demagnetisation. A field of the order of 30,000 oersteds is often employed. The heat of magnetisation is conducted away by the Helium gas to the liquid Helium bath. The container is next evacuated. The salt is magnetised at 1°K, and thermally isolated. Next the magnetic field is switched off and the field is reduced to zero by removing the magnet. The susceptibility is measured. The direct measurment of the low temperature attained after demagnetisation is not possible. That is why the susceptibility is measured and assuming the validity of Curie-Law, the low temperature is calculated. This calculated temperature is not the true Kelvin temperature and is termed the Curie temperature or the magnetic temperature.

Let it be denoted by $\theta_m{}^\circ$.

Then $$\theta_m = \frac{C\mathcal{H}V}{\mathcal{M}} = \frac{C}{\kappa} \text{ (Curie Law)},$$

the magnetic temperature is then converted into Kelvin temperature.

20.3. Conversion of magnetic temperature to Kelvin temperature

We know,

$$TdS = dU - \mathcal{H}d\mathcal{M}$$

Suppose the field is zero and kept constant,

then $$T = \left(\frac{\partial U}{\partial S}\right)_{\mathcal{H}=0} = \frac{\left(\frac{\partial U}{\partial \theta_m}\right)_{\mathcal{H}=0}}{\left(\frac{\partial S}{\partial \theta_m}\right)_{\mathcal{H}=0}} \qquad \ldots (h)$$

where T is the temperature expressed in Kelvin scale. Its value can be obtained by determining the quantities on the right-hand side. These determinations were done in the following way. A quantity of a paramagnetic substance is taken at a known temperature T_i, determined by He-vapour-pressure thermometer. In Fig 20b, the point A determines its initial state. Its entropy at A is S_A (say) and it is under zero magnetic field ($\mathcal{H} = 0$). The graph is made by plotting temperature against field.

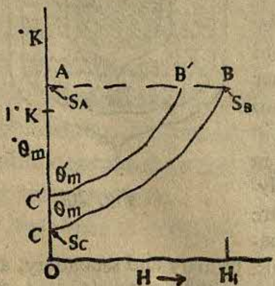


Fig. 20b

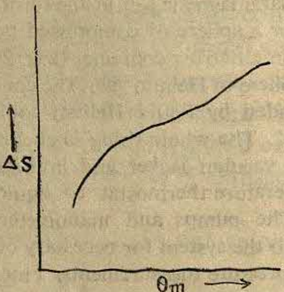


Fig. 20c

It is then magnetised isothermally until the field becomes $\mathscr{H}_i$ from zero. The point B dentotes its magnetised state. Let the entropy now be S_B. By directly measuring the heat-change $\triangle Q$ in the magnetisation, the entropy-rise $S_B - S_A \left(= \dfrac{\triangle Q}{T_i} \right)$ is known.

Then the substance is *adiabatically* demagnetised until the field again becomes zero. The entropy does not change. There will be a drop of temperature when the point C is reached where $(\mathscr{H} = 0)$. The entropy difference between states A and C $= S_C - S_A = S_B - S_A$.

Let the temperature at the point C be T°K or θ_m (magnetic) calculated from susceptibility measurements. It is obvious that θ_m as well as the entropy change $S_C - S_A$ $(= \triangle S)$ would depend upon the applied field $\mathscr{H}_i$. Demagnetising with different initial fields $\mathscr{H}_i$, the different values of θ_m are obtained, the entropy changes $\triangle S$ are then plotted against θ_m as in Fig. 20*c*. This enables the calculation of $\left(\dfrac{\partial S}{\partial \theta_m} \right)_{\mathscr{H}=0}$ which is required in equation (*h*). Finally, at zero field $(\mathscr{H} = 0)$, the paramagnetic substance is heated from θ_m to θ'_m and the heat absorbed is estimated directly. The heat is supplied, say by introducing γ-rays or radiation of a heated filament or from an induction heater etc.

$$\text{Then at } \mathscr{H} = 0, \left(\frac{\triangle Q}{\triangle \theta_m} \right)_{\mathscr{H}=0} = \left(\frac{\partial U}{\partial \theta_m} \right)_{\mathscr{H}=0}$$

By substitution of these quantities in equation (*h*) the magnitude of Kelvin temperature T is known.

20.4. Another interesting fact may be noted. Since $\mathscr{M} = \kappa V \mathscr{H}$ (eqn. 20*a*),

$$\left(\frac{\partial \mathscr{M}}{\partial T} \right)_{\mathscr{H}} = \left(\frac{\partial \kappa}{\partial T} \right)_{\mathscr{H}} ; \text{ therefore } \left(\frac{\partial \kappa}{\partial T} \right)_{\mathscr{H}} = \left(\frac{\partial S}{\partial \mathscr{H}} \right)_T ,$$

from eqn (*d*).

Hence as $T \rightarrow 0$, $\left(\dfrac{\partial \kappa}{\partial T} \right)_{\mathscr{H}} \rightarrow 0$ (Third Law) *i.e.* the susceptibility of all paramagnetic substanes tends to zero.

II. THERMO-ELECTRIC EFFECT

20.5. The Seebeck effect

If two wires of different metals A and B are joined end to end to form a closed circuit, and then, one of the junctions (say P) be heated while the other junction is kept cold, an electric current is produced in the circuit (Fig 20*d*). The flow of electric current means generation of e.m.f. and the production of electric energy in the system, evidently at the expense of the heat received at the hot junction. This is therefore, a *thermo-electric phenomenon* and is commonly called the *Seebeck effect* after the name of its discoverer.

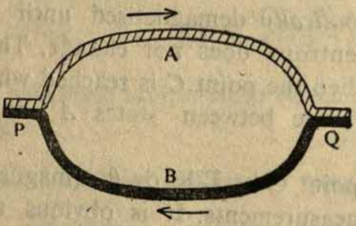


Fig. 20*d* The Seebeck effect.

If instead, the other junction Q be heated and the junction P is kept cold, the current produced would flow in the opposite direction. The process is thus reversible. The magnitude of the thermo-electric e.m.f. produced depends on the nature of the metals taken and the temperature-difference of the two junctions.

From the electron theory. we may say, that within the metals, the electrons like gas molecules are all moving about; their densities in different metals are different. When the two metals are joined, there is a tendency of the electrons moving from a higher to a lower density, giving rise to a potential difference. If both the junctions be at the same temperature, these potential differences counterbalance one another and no current will flow. But if one junction be hotter than another, the transport of electrons across the boundaries would be greater in one than in the other. That is, the potential differences at the two junctions are unequal and a current will flow.

From the study of a large number of metal pairs, Seebeck prepared a graded list of metals to indicate the direction of the thermo-electric current at the hot junction. The list is graded as

Bi. Ni, Co, Pt, Cu, Hg, Pb, Sn, Ag, Zn, Cd, Fe, Sb.

At the hot junction, the current will flow from a metal earlier to the later in the list. The pairs of metals are often termed thermo-electric couples. Thus, in a Cu-Fe couple, the thermo-electric current will flow from Copper to Iron at the hot junction.

The thermo-electric e.m.f. produced is expressed by the empirical relation,

$$E = a\theta + b\theta^2$$

where θ is the temperature difference, a and b are constants. The E-θ relation is a parabola. The maximum e.m.f. is produced at $\frac{dE}{d\theta} = 0$, *i.e.*, when

$$\theta = -\frac{a}{2b} \text{ (Fig. 20}e\text{).}$$

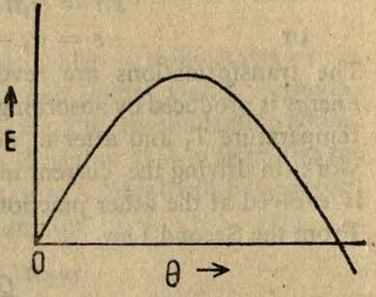


Fig. 20*e*

20.6. The Peltier effect

In 1834, Peltier discovered the opposite phenomenon. He found that if a current flows across a junction of two metals, there was either evolution or absorption of heat, *i.e.*, electric energy is rendered into thermal energy.

In the iron-copper thermocouple, we have seen, the current flows from Cu to Fe at the hot junction due to the Seebeck effect. Now, if both the junctions be kept at the same temperature T and a current is introduced in the circuit as in (Fig 20*f*) in the same direction as was obtained in the Seebeck effect, heat would be absorbed in the junction which was previously hot and heat would be evolved at the other junction. That is, the junction where the current passes from copper to iron will be cold and the other junction will be heated. This is known as the *Peltier effect*.

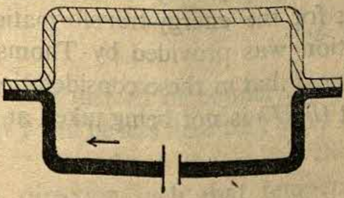


Fig. 20*f*. The Peltier effect.

The amount of energy-change occurring at a junction when unit current passes for unit time is called the Peltier coefficient, π. If q quolombs pass across a junction producing heat-change Q joules, then $Q = \pi q$.

If π_1 and π_2 be the Peltier coefficients at the two junctions of the circuit, then the net energy-change would be $\pi_1 it - \pi_2 it$, where

i is the current across the junction for time t. Again, if e be the net thermo-electric e.m.f. at the junctions, then

$$eit = \pi_1 it - \pi_2 it$$

or

$$e = \pi_1 - \pi_2$$

The transformations are reversible. In a thermocouple electric energy is produced by absorbing heat Q_1 at one junction at a higher temperature T_1 and after a portion of the heat is rendered into work (in driving the current in the circuit) the rest of the heat Q_2 is evolved at the other junction (sink) at a lower temperature T_2. From the Second Law,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Again, from Peltier effect, $\dfrac{\pi_1 it}{\pi_2 it} = \dfrac{Q_1}{Q_2}$

Hence

$$\frac{\pi_1}{\pi_2} = \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

or

$$\frac{\pi_1 - \pi_2}{\pi_2} = \frac{T_1 - T_2}{T_2}$$

or*

$$e = \frac{T_1 - T_2}{T_2}\,\pi_2$$

If the lower temperature-junction be kept at constant temperature (T_2), π_2 will also remain constant. This indicates that the e.m.f. produced will be proportional to the temperature-difference and should increase linearly with $\triangle T$ ($= T_1 - T_2$). But the experimental observations are different. It is found that 'e' rises with temperature-difference, reaches a maximum and then falls, and is ultimately reversed. The relation is parabolic. The Peltier effect then alone cannot account for the energy-transformations in a thermo-couple. The explanation was provided by Thomson (Lord Kelvin). It must be remembered that in these considerations, the irreversible Joule heating effect (i^2RT) is not being taken at all into account.

20.7. Thomson effect

Thomson pointed out that when a current flows in a thermocouple circuit, absorption or evolution of energy does not occur only at the junctions, but the energy is absorbed or evolved all along the conductors due to difference of temperature between the two ends of the same. This is Thomson effect and it is a reversible process.

Consider a thick bar of copper which is heated just at the centre, then the temperature at the two points *x* and *y* equidistant from the centre will be the same, due to conduction alone. Now, if a current be passed in the direction $x \rightarrow y$ (Fig 20*g*) the temperature at *y* will be greater than at *x*. Heat will be absorbed along *xo* and would be evolved along *oy*.

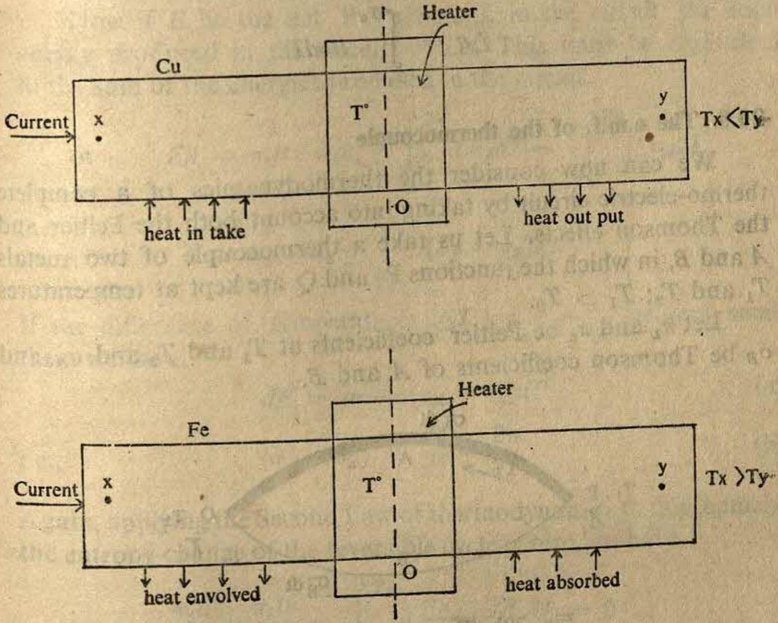


Fig. 20*g*. Thomson effect

If instead of copper, an iron-bar be taken, the temperature at *y* will be less than that at *x*. (The Joule effect is neglected).

This shows that when the current flows in a conductor, in a direction such that temperature decreases and changes from point to point, there will be heat absorption in some metals (such as Fe, Ni, Co, Bi, etc) and heat will be evolved in others (such as Cu, Ag, Zn, Sb, etc). In lead, however, the Thomson effect is nil, and so lead is taken as a standard in thermo-electric studies. In a thermocouple there would be two metals and the energy absorption or evolution along the two conductors due to the Thomson effect would be different. Thus there would also be an e.m.f. in the circuit due to Thomson phenomenon.

The heat-change occurring when unit current flows for unit time between two points differing in temperature by 1°C is called the Thomson-coefficient, σ. The Thomson coefficient is a function of temperature. So, the amount of the thermal change that would occur when i units of current flow for t seconds through a conductor having temperatures T_1 and T_2 at its ends would be

$$\Delta q = \int_{T_1}^{T_2} it\sigma dT$$

20.8. The e.m.f. of the thermocouple

We can now consider the thermodynamics of a complete thermo-electric circuit by taking into account both the Peltier and the Thomson effects. Let us take a thermocouple of two metals A and B, in which the junctions P and Q are kept at temperatures T_1 and T_2; $T_1 > T_2$.

Let π_1 and π_2 be Peltier coefficients at T_1 and T_2 and σ_A and σ_B be Thomson coefficients of A and B.

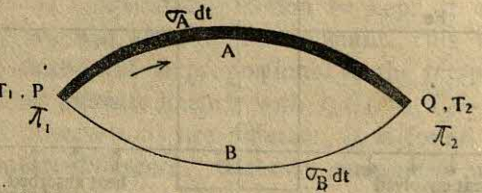


Fig. 20*h*. The e.m.f. of a Thermocouple.

Due to difference in temperatures of the two junctions, electric charge would be flowing through the circuit in directions as noted in the figure 20*h*. The energies would be absorbed or evolved at the junctions (Peltier) as also along the conductor (Thomson).

Then, for Peltier effect,

the energy absorbed at P $= it\pi_1$ (absorption)

the energy absorbed at Q $= -it\pi_2$ (evolution)

and for Thomson effect,

the energy absorbed by A from T_1 to T_2 $= \int_{T_1}^{T_2} it\ \sigma_A dT$

the energy absorbed by B from T_2 to T_1 $= \int_{T_2}^{T_1} it\ \sigma_P dT$

$$= -\int_{T_1}^{T_2} it\ \sigma_B dT$$

when current i flows for t seconds.

Now if E be the net thermo-e.m.f. in the circuit, the total energy produced in the circuit $= Eit$. This must be equivalent to the sum of the energies produced in the circuit.

or
$$Eit = \pi_1 it - \pi_2 it + \int_{T_1}^{T_2} it\ \sigma_A dT - \int_{T_1}^{T_2} it\ \sigma_B dT$$

or
$$E = \pi_1 - \pi_2 + \int_{T_1}^{T_2} (\sigma_A - \sigma_B) dT$$

If the difference of temperatures $\triangle T$ ($= T_1 - T_2$) be very small then, we have,

$$dE = d\pi + (\sigma_A - \sigma_B) dT \qquad \ldots \text{(a)}$$

i.e.,
$$(\sigma_A - \sigma_B) = \frac{dE}{dT} - \frac{\partial \pi}{\partial T} \qquad \ldots \text{(b)}$$

Again, applying the Second Law of thermodynamics to this, namely, the entropy-change of the reversible cycle is zero, we have,

$$\frac{\pi_1 it}{T_1} - \frac{\pi_2 it}{T_2} + \int_{T_1}^{T_2} it\, \frac{\sigma_A - \sigma_B}{T}\, dT = 0$$

or
$$\partial \left(\frac{\pi}{T}\right) + \frac{\sigma_A - \sigma_B}{T}\, dT = 0 \qquad \ldots \text{(c)}$$

Hence
$$\frac{\partial \pi}{T} - \frac{\pi}{T^2}\, dT + \frac{(\sigma_A - \sigma_B)}{T}\, dT = 0$$

or
$$T \frac{\partial \pi}{\partial T} - \pi + T\,(\sigma_A - \sigma_B) = 0$$

or
$$\pi = T\left(\frac{\partial \pi}{\partial T}\right) + T\,(\sigma_A - \sigma_B) \qquad \ldots \text{(d)}$$

Substituting (*b*) in (*d*), $$\pi = T\frac{\partial E}{\partial T} \qquad \ldots \text{(i)}$$

or $$\frac{\partial \pi}{\partial T} = \frac{\partial E}{\partial T} + T\frac{\partial^2 E}{\partial T^2}$$

Substituting in (*b*),

$$\sigma_A - \sigma_B = \frac{\partial E}{\partial T} - \frac{\partial \pi}{\partial T} = -T\frac{\partial^2 E}{\partial T^2} \qquad \ldots \text{(ii)}$$

In equations (*i*) and (*ii*) we obtain the thermodynamic expressions for Peltier and Thomson effects. The values of π and σ are calorimetrically determined, and *E*, the e.m.f. is potentiometrically measured. Experimental corroborations of these equations have been tested, as would be seen from the following data.

TABLE : PELTIER AND THOMSON EFFECTS

Couple	$\frac{\pi}{T} \times 10^6$	$\frac{\partial E}{\partial T} \times 10^6$	$\frac{\sigma_2 - \sigma_1}{T} \times 10^8$	$\frac{\partial^2 E}{\partial T^2} \times 10^8$
Cu−Fe	−10.16	−10.1	2.1	2.7
Cu−Ni	18.9	18.8	6.0	6.3

The thermo-electric effect is utilised in measuring small rise in temperature caused by radiations. Suitable thermocouples are often joined in series to form a thermopile and the e.m.f. produced by the radiations at the junctions can be registered through a sensitive galvanometer.

For accurate estimations of temperature thermoelectric pyrometers, which are truly thermocouples, are used. The radiomicrometers for detection of radiations are also constructed with thermocouples.

III. THE THERMIONIC EFFECT

20.9. The Thermionic effect

It is well-known that if a metallic conductor is heated strongly, specially at a low pressure or vacuum, negatively charged particles are emitted. These particles have been identified to be electrons. The phenomenon is known as *thermionic emission*. It can be very simply explained from the electron theory. In the metals we have a large preponderence of electrons moving swiftly at random.

Application of heat causes a rapid increase in the energy of the moving electrons, such that some of these are shot out from the surface and emission occurs. At a given temperature however very soon an equilibrium would be attained. The number of electrons emitted per second would be the same as that returning to the metal.

A quantitative treatment of this phenomenon requires not only thermodynamic principles but also application of some of the concepts of the kinetic theory. We may proceed in the following way, as initiated by Richardson.

(*i*) The electrons are discrete particles and the electrons present in the surroundings of a heated conductor may be taken as an electron gas, obeying the ideal gas laws. Then the pressure of the electron gas $p = nkT$ . . . (a)

where n = no. of electrons per c.c. at temperature T

and k = Boltzmann constant, R/N.

(*ii*) The electrons emitted are in equilibrium with the electrons in the solid metal at temperature T; the process is analogous to sublimation. Hence thermodynamically,

$$dS = \frac{\delta Q}{T} = \frac{dU + pdV}{T}$$

where, PdV = external work performed, for the process of emission. Let us say, ϕ = energy-change in the emission of a single electron. We may call ϕ as the latent heat of emission of an electron.

Then energy-change, $dU = d(n.v\phi)$ . . . (b)

where v is the volume of the system enclosing the electrons.

Under conditions of equilibrium and at a constant temperature, n and ϕ are constant, hence $\left[\frac{\partial(n\phi)}{\partial v}\right]_T = 0.$

[*cf.* $\left(\frac{dU}{dV}\right)_T$, for an ideal gas, is zero].

Now,
$$dS = \frac{dU + pdv}{T} = \frac{1}{T}\, d(nv\phi) + \frac{p}{T}dv$$

$$= \frac{1}{T}\, n\phi dv + \frac{v}{T}d(n\phi) + \frac{p}{T}dv$$

$$= \frac{1}{T}\, [n\phi + p]dv + \frac{v}{T}\left[\left(\frac{\partial(n\phi)}{\partial v}\right)_T dv + \left(\frac{\partial(n\phi)}{\partial T}\right)_v dT\right]$$

$$= \frac{1}{T}[n\phi + p]dv + \frac{v}{T}\left[\frac{\partial(n\phi)}{\partial T}\right]_v dT$$

Hence $\left(\frac{\partial S}{\partial v}\right)_T = \frac{1}{T}(n\phi+p)$; $\left(\frac{\partial S}{\partial T}\right)_v = \frac{v}{T}\left(\frac{\partial n\phi}{\partial T}\right)_v$

$$\therefore\quad \frac{\partial^2 S}{\partial v \partial T} = -\frac{(n\phi)}{T^2} + \frac{1}{T}\frac{\partial(n\phi)}{\partial T} - \frac{p}{T^2} + \frac{1}{T}\frac{\partial p}{\partial T}$$

and
$$\frac{\partial^2 S}{\partial T \partial v} = \frac{1}{T}\frac{\partial(n\phi)}{\partial T} - \frac{v}{T^2}\frac{\partial(n\phi)}{\partial T}\cdot\frac{\partial T}{\partial v} + \frac{v}{T}\frac{\partial^2(n\phi)}{\partial T \partial v}$$

$$= \frac{1}{T}\frac{\partial(n\phi)}{\partial T}\left(\text{since } \frac{\partial(n\phi)}{\partial v} = 0\right)$$

Equating the two, $\frac{1}{T}\frac{\partial p}{\partial T} = \frac{n\phi}{T^2} + \frac{p}{T^2}$

or, $$T\frac{dp}{dT} = p + n\phi \qquad \text{. . . (c}$$

Since $p = nkT$, $$T\frac{d(nkT)}{dT} = nkT + n\phi$$

or, $$nkT + kT^2\frac{dn}{dT} = nkT + n\phi$$

or, $$kT^2\frac{dn}{dT} = n\phi$$

or, $$\frac{dn}{n} = \frac{\phi}{kT^2}\,dT \qquad \text{. . . (d')}$$

i.e., $$n = A_1 e^{\int \frac{\phi}{kT^2}dT} \qquad \text{. . . (d)}$$

where A_1 is a constant.

In a gas, according to the kinetic theory, the number of gas molecules n' returning to the surface per second is given by

$$n' = n\sqrt{\frac{kT}{2\pi m}}$$

where n is the number of molecules present per c.c. of the gas and m is the mass of a molecule. Applying this to the electron gas and remembering that in equilibrium the number of electrons emitted per second equals the number returning to the conductor, we can write, No. of molecules emitted, $\bar{N} = n' = n\sqrt{\dfrac{kT}{2\pi m}}$

$$= A_1\, e^{\int \frac{\phi}{kT^2}dT} \sqrt{\frac{kT}{2\pi m}} = A_1 \sqrt{\frac{k}{2\pi m}}\; T^{\frac{1}{2}}.e^{\int \frac{\phi}{kT^2}dT}$$

$$= A_2 T^{\frac{1}{2}} e^{\int \frac{\phi}{kT^2}dT} \qquad \ldots \text{(e)}$$

This relation is approximate, for it has been assumed that ϕ is not dependent on temperature, which is not necessarily true. When temperature is raised say from 1000° to 2000°C, the energy-change ϕ associated with the emission of an electron cannot be the same. To find a more accurate expression, Richardson later introduced the thermodynamical relations in a novel way.

Suppose two *identical* spherical conductors, A and B are enclosed in vacuum in two chambers at temperatures T and T' (Fig 20*i*). When electron-emission takes place, let the potentials at the surfaces of A and B, be V and V' respectively. As we recede from the surface of A, the potential will gradually fall and let the potential at C be V', the same as that of the surface of B. Imagine that A is surrounded by an enclosure at C of constant potential equal to V'. Let the pressures due to electrons (considered as electron gas) at the surfaces of A and B be denoted by p and p' and let the pressure at the constant potential enclosure be p_0.

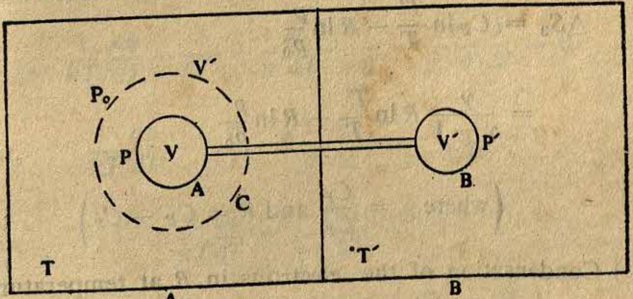


Fig. 20*i* Richardson's Thermionic emission

We can now imagine a complete reversible cycle carried out in the following way :

(*i*) Let Avogadro's number of electrons (N_0) be emitted from A, (*ii*) these electrons are carried from the surface of A (presure p, potential V) to the constant potential enclosure at C (pressure p_0, potential V'), (*iii*) the electrons are then transferred to the surface of B at the same potential from a pressure p_0 and temperature T to a pressure p' and temperature T', (*iv*) from B, the electrons are allowed to flow back to the surface of A through a thin metallic conductor. All the steps are reversible.

We can calculate the entropy-changes in the different steps of the process, as :

(*i*) emission of electrons at A ; $\triangle S_1 = \dfrac{N_0\phi + RT}{T}$

(where ϕ = latent heat at T)

(*ii*) Transfer of electrons from A to C;

$$\triangle S_2 = \frac{Q(V-V')}{T} \approx \frac{RT \ln p/p_0}{T} \approx R \ln p/p_0$$

(where Q = total charge of the electrons)

(*iii*) Transfer of electrons at constant potential from C to B;

$$\triangle S_3 = C_P \ln \frac{T'}{T} - R \ln \frac{p'}{p_0}$$

$$= \frac{\gamma}{\gamma-1} R \ln \frac{T'}{T} - R \ln \frac{p'}{p_0}$$

$$\left(\text{where } \gamma = \frac{C_P}{C_v} \text{ and } R = C_P - C_v\right)$$

(*iv*) Condensation of the electrons in B at temperature T';

$$\triangle S_4 = -\frac{N_0\phi' + RT'}{T'} \quad (\text{where } \phi' = \text{latent heat at } T')$$

(*v*) Transfer of electrons from B to A along a metallic conductor from temperature T' to T, σ = Thomson coefficient of the conductor,

$$\triangle S_5 = \int_{T'}^{T} \frac{Q\sigma}{T}\, dT$$

Then the net entropy-change of the *reversible cyclic* process,

$$\frac{N_0\phi+RT}{T}+R\ln\frac{p}{p_0}+\frac{\gamma}{\gamma-1}R\ln\frac{T'}{T}-R\ln\frac{p'}{p_0}-\frac{N_0\phi'+RT'}{T'}+\int_{T'}^{T}\frac{Q\sigma dT}{T}=\Delta S=0$$

Rearranging, and neglecting the last term which is indeed very small, we have,

$$\frac{N_0\phi}{T}-\frac{N_0\phi'}{T'}+R\ln p-R\ln p'-\frac{\gamma}{\gamma-1}R\ln T+\frac{\gamma}{\gamma-1}R\ln T'=0$$

Dividing by N_0 and transposing,

$$\frac{\phi}{T}+k\ln p-\frac{\gamma}{\gamma-1}k\ln T=\frac{\phi'}{T'}+k\ln p'-\frac{\gamma}{\gamma-1}k\ln T'=\ldots=Z_1 \quad \text{(const.)}.$$

$$\text{or,}\quad \frac{\phi}{kT}+\ln(nkT)-\frac{\gamma}{\gamma-1}\ln T=\frac{Z_1}{k}=Z_2\ \text{(const.)}.$$

Differentiating,

$$\frac{1}{kT}\frac{d\phi}{dT}-\frac{\phi}{kT^2}+\frac{1}{n}\frac{dn}{dT}+\frac{1}{T}-\frac{\gamma}{\gamma-1}\frac{1}{T}=0$$

$$\text{or,}\quad \frac{1}{kT}\frac{d\phi}{dT}-\frac{\phi}{kT^2}+\frac{1}{n}\frac{dn}{dT}-\frac{1}{\gamma-1}\frac{1}{T}=0$$

$$\text{or,}\quad \frac{1}{kT}\frac{d\phi}{dT}=\frac{1}{\gamma-1}\frac{1}{T}$$

$$\left(\text{since from } (d'),\text{ we have } \frac{1}{n}\frac{dn}{dT}=\frac{\phi}{kT^2}\right)$$

$$\text{or,}\quad \frac{d\phi}{dT}=\frac{k}{\gamma-1}=\frac{k}{5/3-1}=\tfrac{3}{2}k$$

The electron gas considered as monatomic, $\gamma=\frac{5}{3}$.

$$\text{or}\quad \phi=\tfrac{3}{2}kT+\phi_0 \qquad \ldots\text{(f)}$$

where the integration constant ϕ_0 is really the latent heat of emission at $T = 0°\text{K}$. Substituting the value of ϕ in equation (*e*), the number of electrons emitted would be

$$\bar{N} = A_2T^{\frac{1}{2}}e^{\int\frac{\frac{2}{3}kT+\phi_0}{kT^2}dT} = A_2T^{\frac{1}{2}}e^{\int\frac{3}{2T}dT}e^{\int\frac{\phi_0}{kT^2}dT}$$

$$= AT^{\frac{1}{2}}T^{\frac{3}{2}}e^{\int\frac{\phi_0}{kT^2}dT} = AT^2e^{\int\frac{\phi_0}{kT^2}dT} \qquad \ldots \text{(g)}$$

If there be a positive anode which would receive and take away the emitted electrons, then the thermionic current would be measured by the charge removed per unit time. Thus the thermionic current i, is given by

$$i = \bar{N}\epsilon = A.\epsilon.T^2e^{\int\frac{\phi_0}{kT^2}dT} = A_0T^2e^{-b/T}$$

where $A_0 = A.\epsilon$ and $b = \phi_0/k$.

This is the well-known *Richardson equation* for thermionic current. The equation may be written as

$$\ln i - 2\ln T = -\frac{b}{T} + \ln A_0 \qquad \ldots \text{(h)}$$

$\therefore$ $\log_e i - 2\log_e T$ plotted against $\frac{1}{T}$ would give a straight line. This has been verified by Richardson and later on, by Langmuir and others. The slope of the line gives the value of b; hence ϕ_0 is known.

Let ψ be the potential at which emission of an electron takes place from a metal. Then, the work of removing N_0 (Avogadro number) electrons would be $\psi \times \mathscr{F}$ (faraday). The energy associated with emission would be $N_0\phi_0 = N_0bk$.

$$\therefore \quad \psi \times \mathscr{F} = N_0bk$$

$$\text{or} \quad \psi = \frac{b \times R}{\mathscr{F}} = \frac{8.4 \times b}{96500} \approx 8.6 \times 10^{-5}\, b$$

Since b is known, the potentials at which emission of electrons takes place from different metals are known, say,

$$\psi_{Ni} = 4.52\ ;\ \psi_{Th} = 3.38\ ;\ \psi_C = 4.3\ ;\ \psi_{Na} = 1.82, \text{ etc.}$$

ψ is obviously a measure of the affinity of the electrons with metal atoms. Emission is a characteristic property of the metal.

IV. THE STRETCHING OF A WIRE

20.10. The process of reversible stretching of a wire under tension may be treated thermodynamically. Let us consider a wire of length l_0 at temperature T stretched by a small amount dl under a tension F. The work done on the system,

$$w = -Fdl$$

The surrounding pressure remains constant and the change in volume is negligible, hence, we have,

$$TdS = q = dU - Fdl = C_F dT - Fdl$$

Applying the TdS equation (eqn. 7.1), we may write

$$TdS = C_F dT + T\left(\frac{\partial l}{\partial T}\right)_F dF$$

Without introducing any appreciable error, as a first approximation, we can replace the heat-capacity at constant tension (C_F) by heat-capacity at constant pressure (C_P), and also $\left(\frac{\partial l}{\partial T}\right)_F$ by $\left(\frac{\partial l}{\partial T}\right)_P$. Thus,

$$TdS = C_P dT + T\left(\frac{\partial l}{\partial T}\right)_P dF \qquad \ldots \text{(a)}$$

Further, the liner expansivity, $\alpha_0 = \frac{1}{l_0}\left(\frac{\partial l}{\partial T}\right)_P$

and the Young's modulus, $Y = \frac{l_0}{a}\left(\frac{\partial F}{\partial l}\right)$

(where a = cross-section of the wire)

Substituting, $TdS = C_P dT + T.a.\alpha_0 Y\left(\frac{\partial l}{\partial F}\right) dF \qquad \ldots \text{(b)}$

In a sudden stretching of the wire, *i.e.*, in adiabatic process ($TdS = 0$).

$$\therefore\ C_P dT = -Ta\alpha_0 Y\left(\frac{\partial l}{\partial F}\right) dF$$

$$\text{or}\quad \frac{dT}{dF} = -\frac{Ta\alpha_0 Y}{C_P}\frac{dl}{dF}$$

$$\text{or}\quad \frac{dT}{dl} = -\frac{Ta\alpha_0 Y}{C_P}$$

Since for metals all the quantities are positive on the right hand side, so $\frac{dT}{dl}$ is negative. That is, in adiabatic stretching, there would be a drop in temperature.

Problem : Calculate the drop in temperature if, at 27°C, a steel wire 100 cm long and 2 mm in diameter is suddenly stretched by 0.1 mm. Given density = 7.8 gm per c.c.

Specific heat = 0.115 cal. per gm ; $\alpha_0 = 1.2 \times 10^{-5}$ per °C,

$$Y = 2\times 10^{12} \text{ dynes/cm}^2$$

Heat capacity of the wire $C_P = 100\times a\times 7.8\times 0.115\times 4.2\times 10^7$ ergs

Hence $$\Delta T = -\frac{300\times a\times 1.2\times 10^{-5}\times 2\times 10^{12}}{100\times a\times 7.8\times 0.115\times 4.2\times 10^7}\times 0.01 = -0.02°\text{C}$$

V. SYSTEM IN GRAVITY FIELD

20-11. The free energy (G) of a substance in a gravity field depends upon its position along vertical height, h. Keeping all other factors constant, if a mole of a substance be raised through a height dh, the change in G, is

$$dG = Mgdh$$

or $$\left(\frac{\partial G}{\partial h}\right)_{P,T,\ldots} = Mg \qquad \ldots (A)$$

Now take a vertical column of pure liquid. Then, $\bar{G}$, will be the same at any point. In the lower part of the column the molal Gibbs energy will be less due to influence of gravity, but it will be higher due to hydrostatic pressure. These two neutralise one another so as to keep G constant. We may say, in this case $\bar{G}$ depends upon position in the gravitational field (h) and upon pressure (P), temperature, etc. remaining constant.

$$\therefore \quad dG = \left(\frac{\partial G}{\partial h}\right)_{P,T,\ldots} dh + \left(\frac{\partial G}{\partial P}\right)_{P,T,\ldots} dP$$

(from A) $$= Mgdh + vdP$$

At eqm, $$Mgdh + vdp = 0$$

or $$\frac{\partial P}{\partial h} = -\frac{Mg}{v} = -\rho g \qquad \ldots (B)$$

(ρ, the density)

When this is extended to a gas, say atmosphere,

$$\frac{dP}{dh} = -\frac{MgP}{RT}$$

$$\text{or} \quad d \ln P = -\frac{Mg}{RT}\, dh$$

$$i.e., \quad \ln \frac{P}{P_0} = -\frac{Mg}{RT}(h-h_0) = -\frac{Mgh}{RT}, \quad \text{since } h_0 = 0$$

$$\text{Hence} \quad P = P_0 e^{-Mgh/RT} = P_0 e^{-\epsilon_{Pot}/RT}$$

This is the well-known Barometric formula.

VI. REACTIONS IN BIOLOGICAL SYSTEMS AND THERMODYNAMICS

20.12 The Coupled Reactions in Metabolic Processes

The transformations, in which the free energy decreases, occur spontaneously. So far, in our observations, only an isolated reaction was considered. In biological systems however, very often, reactions are found to occur spontaneously in which free energy increase would be involved. The reactions with increase in energy are *endoergonic reactions*. But these reactions in bio-systems do not occur individually or in an isolated way. Generally a number of reactions, mutually dependent upon one another, take place simultaneously. To take a simple case, an endoergonic reaction is always associated or coupled with a reaction in which free energy decreases (i.e., *exoergonic reaction*). When the free energy decrease in an exoergonic reaction is greater than the free energy increase of a desirable endoergonic reaction, the coupling of the two processes would have a negative ΔG to make the reactions spontaneous. The result of coupling in metabolic processes is that a reaction, which is desirable but energetically improbable, is induced to happen by linking it with a reaction which is spontaneous and liberates a larger amount of free energy. Such a coupled reaction would occur only when the two reactions have a common reactant or product. In bio-systems, the molecule adenosine triphosphate, called *ATP*, is the most common coupling agent.

The structures of *ATP* is given here.

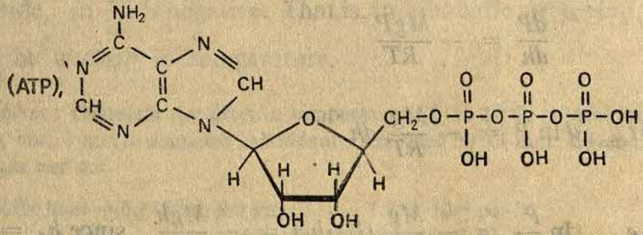


Fig 20*f*. Adinosine triphosphate (*ATP*) formed from adenine base, ribose sugar and three phosphate groups. The last two phosphate bonds have high free energy of formation and thus serve as a store of chemical energy for living processes.

The transformation of *ATP* to *ADP* (adenosine diphospate) is an exoergonic process :

$$ATP + H_2O \rightarrow ADP + HPO_4^{--} + H^+ \; ; \; \triangle G^0 = -7.1 \text{ kcal}$$

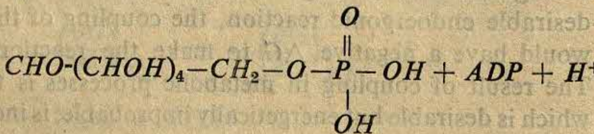
Hence, if this change is associated with an endoergonic metabolic or synthetic process (in which *ATP* also participate s), the coupled reaction might easily be an one with net free energy decrease and be spontaneous.

As an illustration, the synthesis of sucrose from glucose and fructose may be cited. The transformation, considered singly is endoergonic.

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \rightarrow \underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \; ; \; \triangle G^0 = +5.5 \text{ kcal}$$

Individually, this transformation is not probable. In fact, this change has been rendered possible in nature by coupling it with a change of *ATP*, as follows:

(*A*) $\underset{\text{glucose}}{CHO\text{-}(CHOH)_4\text{-}CH_2OH} + ATP \rightarrow$



$$CHO\text{-}(CHOH)_4-CH_2-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH + ADP + H^+$$

glucose—6—phosphate

(*B*) Glucose—6—phosphate + fructose → sucrose + HPO_4^{--}

The sum of the two processes (*A*) and (*B*) is really a couple of reactions in which not only sucrose is formed but *ATP* is also transformed into *ADP*. The net free energy change of the coupled process is

$$\triangle G^0_{\text{net}} = (5.5 - 7.1) \text{ kcal}$$
$$= -1.6 \text{ kcal}$$

That is why the coupled reaction has become spontaneous.

Problems

1. Prove that for a paramagnetic substance obeying Curie's Law ;

(*i*) $\left(\frac{\partial U}{\partial M}\right)_T = \mathscr{H} - T\left(\frac{\partial \mathscr{H}}{\partial T}\right)_M$

(*ii*) $\left(\frac{\partial U}{\partial \mathscr{H}}\right)_T = 0$

2. For an isoentropic change in a magnetic field, show

$$T_1^2 - T_2^2 = 2QT_1/C_{\mathscr{H}}$$

where Q is the heat effect for an isothermal change with the same change of field.

3. Show that for a Curie solid, the heat transfer for an isothermal process is given by

$$Q = -K(\mathscr{H}_f^2 - \mathscr{H}_i^2)/2T$$

4. Consider the electron gas as monatomic and ideal and its specific heat in the condensed state is negligible. Show that in thermionic emission, its equilibrium pressure can be expressed as

$$\ln p_e = -\lambda_0/RT + \tfrac{5}{2}\ln T + \text{constant}$$

and that the saturation current

$$i = A_0T^2e^{-\lambda_0/RT}$$

[Use formula for vap-pressure constant]

5. One meter of steel wire (1 mm diameter) is stretched isothermally at 27°C from zero to 10^8 dynes. Calculate the heat transferred in joules if

$$Y = 2\times10^{12} \text{ dynes/cm}^2,\ \alpha = 1.2\times10^{-5} \text{ deg}^{-1}$$
$$C_P = 0.115 \text{ cal/gm},\ \rho = 7.86 \text{ gm/cm}^3$$

6. A paramagnetic salt, obeying Curie's Law, is cooled to 3°K in liquid helium. It is then magnetised isothermally and then demagnetised adiabatically. During isothermal magnetisation 5×10^{-3} joules of heat was removed. Estimate the final temperature after demagnetisation, if the total heat capacity, $C_H = 10^{-3}T^3$ joules/degree. [Ans. 2.785°K]

CHAPTER 21

DETERMINATION OF ACTIVITY AND ACTIVITY COEFFICIENT

The terms, activity and activity coefficient, have been frequently used in connection with the study of different types of equilibria. Some of the methods employed to determine these quantities may now be considered.

21.1. The vapour pressure method

(*a*) *The activity of the solvent*. The activity of the solvent in a solution can be easily ascertained from a knowledge of its vapour pressure. Let the vapour pressure of the solvent over the given solution be P_1 and that over the pure state of the solvent be $P_1{}^0$. If the vapour pressures be not high and the vapours behave more or less like ideal gases, the vapour pressures may be taken as the fugacities of the solvent in the respective states, denoted by $\mathbf{f}_1$ and $\mathbf{f}_1{}^0$. So, we can write the activity of the solvent in the solution, as

$$a_1 = \frac{\mathbf{f}_1}{\mathbf{f}_1{}^0} = \frac{P_1}{P_1{}^0} \qquad \ldots (21.1)$$

At any given temperature, the vapour pressure $(P_1{}^0)$ at the standard state which is the pure liquid is constant. In fact, $1/P_1{}^0$ is the conversion factor of P_1 to obtain the activity.

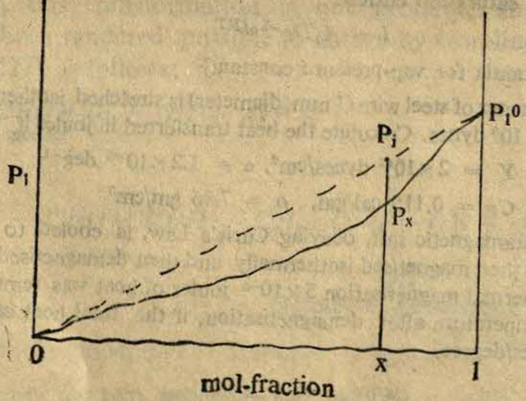


Fig. 21*a*. Activity of solvent from vapour pressure

In fig. 21*a*, the actual vapourpressures of the solvent over the solution are plotted, by the solid line, against the mol-fractions of the solvent. The broken line denotes the Raoult's law relation for the ideal solution. At a concentration of the solution (mol-fraction x), let the observed vapour pressure be P_x and the ideal vapour pressure be P_i. The vapour pressure of the pure liquid is $P_1{}^0$ (at $N_1 = 1$). Then, the activity of the solvent in the solution, would be

$$a_1 = \frac{P_x}{P_1{}^0}.$$

If the solute be a liquid completely miscible with the solvent and is not very volatile, the standard state of the solute may be taken as its pure liquid state. The activity of the solute, in such an event, may then be determined in the same way as that for the solvent.

(*b*) *The activity of the volatile solute* : The activity of the volatile solute, a_2, in dilute solutions can also be determined from vapour pressure data. If P_2 and $\mathbf{f}_2$ be the partial pressure and fugacity of the solute in a dilute solution having a concentration of mol-fraction, N_2, then,

$$a_2 = \frac{\mathbf{f}_2}{k_2} \approx \frac{P_2}{k_2}, \text{ where } k_2 \text{ is a constant.}$$

In very dilute solutions ($Lt.\ N_2 \rightarrow 0$),

$$a_2{}^* = N_2{}^*$$

where $a_2{}^*$ is the activity in the highly dilute solution of mol-fraction $N_2{}^*$. Hence

$$N_2{}^* = \frac{P_2{}^*}{k_2}, \quad i.e., \ k_2 = \frac{P_2{}^*}{N_2{}^*}.$$

So, the activity of the solute in the given solution would be,

$$a_2 = \frac{P_2}{k_2} = P_2 \Big/ \frac{P_2{}^*}{N_2{}^*} \qquad \ldots (21.2)$$

and the activity coefficient $\gamma_{N_2} = \dfrac{P_2}{N_2} \Big/ \dfrac{P_2{}^*}{N_2{}^*}$ ... (21.3)

When the solute is volatile enough to permit experimental determination of its partal vapour pressures P_2 at different mol fractions (N_2), the method can be employed to detrmine γ_2. In fact, P_2/N_2

is plotted against N_2 and on extrapolation to $N_2 = 0$, the value of P_2^*/N_2^* (*i.e.*, k_2)is obtained. From equations 21.2 and 21.3 the activity and activity coefficients are calculated.

Problem : An aqueous solution has the partial vapour pressure of water 18.49 mm at 25°C. What is the activity of water in this solution?

The vapour pressure of pure water (standard state) is the unit of activity. The vapour pressure of pure water at 25°C = 23.55 mm.

$$\therefore \text{ activity of water in the solution} = \frac{18.49}{23.55} = 0.785$$

21.2. Determination of the activity of one component from that of the other component

In a binary solution, containing N_1 and N_2 mol-fractions of the two components,

$$N_1 d\mu_1 + N_2 d\mu_2 = 0$$

or
$$N_1 RT d\ln a_1 + N_2 RT\, d\ln a_2 = 0$$

or
$$N_1\, d\ln a_1 + N_2\, d\ln a_2 = 0 \qquad \ldots (A)$$

Again, $N_1 + N_2 = 1$, or $dN_1 + dN_2 = 0$

$$\therefore \qquad N_1 \frac{dN_1}{N_1} + N_2 \frac{dN_2}{N_2} = 0$$

or
$$N_1\, d\ln N_1 + N_2\, d\ln N_2 = 0 \qquad \ldots (B)$$

Subtracting (B) from (A), we have a general relation between the activities of the components and the composition,

$$\left.\begin{aligned} N_1\, d\ln \frac{a_1}{N_1} + N_2\, d\ln \frac{a_2}{N_2} &= 0 \\ \text{or,} \quad N_1\, d\ln \gamma_1 + N_2\, d\ln \gamma_2 &= 0 \end{aligned}\right\} \qquad \ldots (21.4)$$

where γ-terms are the activity coefficients on mol-fraction basis.

(*i*) *Activity of the solvent from that of the solute* : Rewriting equation (21.4),

$$d\log \frac{a_1}{N_1} = -\frac{N_2}{N_1}\, d\log \frac{a_2}{N_2}$$

$$i.e., \quad \log \frac{a_1}{N_1} = -\int_{N_2=0}^{N_2} \frac{N_2}{N_1}\, d\log \frac{a_2}{N_2} \qquad \ldots (21.5)$$

(The limits are given as N_2 for easy understanding.)

Now, $\log \gamma_2$ (*i.e.*, $\log \frac{a_2}{N_2}$) which is known from a separate determination is plotted against $\frac{N_2}{N_1}$ from zero concentration to the mol-fraction N_2. The area under the curve gives the value of the integral in the right-hand side (Fig. 21*b*). Thus, $\frac{a_1}{N_1}$, and therefore a_1, for the solvent is known from the activity of the solute.

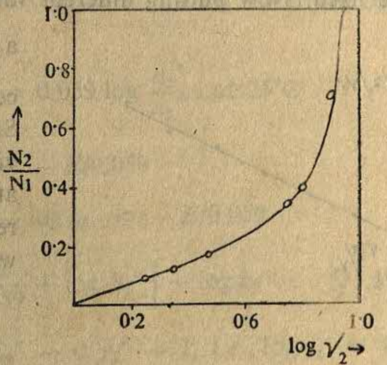


Fig. 21*b*. Determination of the activity of the solvent from that of the solute.

(*ii*) *Activity of the solute from that of the solvent* : Again, from the relation (21.4),

$$d \ln \gamma_2 = -\frac{N_1}{N_2}\, d \ln \gamma_1 \qquad \ldots (21.6)$$

We know as N_2 approaches zero, $\gamma_2 \rightarrow 1$, *i.e.*, $\ln \gamma_2 \rightarrow 0$.

Therefore, integration of this relation between zero and N_2 mol-fractions of the solute, changing the logarithm, would give

$$\log \gamma_2 = -\int_0^{N_2} \frac{N_1}{N_2}\, d \log \gamma_1 \qquad \ldots (21.7)$$

The graphical integration of the right-side is not possible for, in infinitely dilute solutions as N_2 approaches zero, $\frac{N_1}{N_2}$ tends to infinity when the evaluation cannot be made.

It is therefore necessary to proceed in a different way. Consider a sufficiently dilute solution instead of the infinitely dilute solution. Let the mol-fraction, activity and activity-coefficient of the solute in this solution be N_2', a_2' and γ_2'. So, from equation (21.6),

$$\log \frac{\gamma_2}{\gamma_2'} = -\int_{N_2'}^{N_2} \frac{N_1}{N_2}\, d \log \gamma_1 \qquad \ldots (21.8)$$

This equation can easily be graphically evaluated as the limits are fixed. Now putting different values of N_2, keeping N_2' fixed, a set of values for $\frac{\gamma_2}{\gamma_2'}$ can be computed from equation (21.8). Suppose γ_2^0 denotes the activity coefficient of the solute at infinite dilution, which is really equal to unity. We can write,

$$\gamma_2 = \frac{\gamma_2}{\gamma_2'} \cdot \frac{\gamma_2'}{\gamma_2^0} = \frac{\gamma_2}{\gamma_2'} \Big/ \frac{\gamma_2^0}{\gamma_2'} \quad \ldots (21.9)$$

If the computed values of γ_2/γ_2' (from equation (21.8) be plotted against N_2 and the same is extrapolated to $N_2 = 0$, we shall obtain the value of γ_2^0/γ_2'. Substituting this in equation 21.9 γ_2 may be calculated. Thus, from a knowledge of the activity of the solvent, the activity of the solute can be found out.

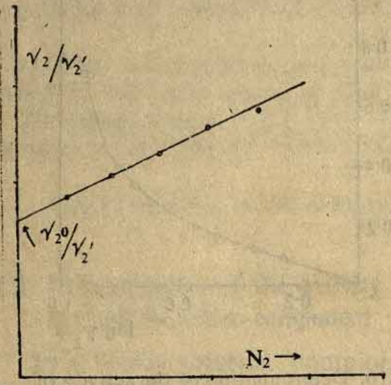


Fig. 21c. Plot of γ_2/γ_2' vs. N_2

21.3. The electromotive force method

The measure of the e.m.f. of cells has also been profitably utilised in determining the activity of electrolytes as well as non-electrolytes.

(*i*) *Non-electrolytes* : The activities of metals used as electrodes in the form of amalgams have often been determined from e.m.f. measurements. Consider an amalgam-electrode cell of the type,

$$\underset{\text{I}}{\text{Li-(Hg)}_x} - \text{Li-salt Soln.} - \underset{\text{II}}{\text{Li-(Hg)}_y}$$

in which two lithium-amalgam electrodes at different concentrations as given below are used.

Electrode	I	II
Concentration (mol-fractions)	N_2'	N_2''
activities	a_2'	a_2''
activity coefficients	γ_2'	γ_2''

For the passage of one faraday of electricity, one gm-atom of lithium would be transported from one electrode to the other.

The change in the free energy would be

$$\triangle G = RT \ln \frac{a_2''}{a_2'} = -n\mathscr{F}E; \quad (E\text{=e.m.f. of the cell})$$

$$\therefore \ -E = \frac{RT}{n\mathscr{F}} \ln \frac{a_2''}{a_2'} = 0.059 \log \frac{a_2''}{a_2'}, \ \text{at } 25°\text{C}$$

Rewriting, $\log a_2'' - \log a_2' = -E/0.059$

or $\log N_2'' + \log \gamma_2'' - \log a_2' = -E/0.059$

or $$\log \gamma_2'' = -\left[\frac{E}{0.059} + \log N_2''\right] + \log a_2' \ldots (21.10)$$

In very dilute amalgams, $Lt.N_2'' \rightarrow 0, \gamma_2'' \rightarrow 1$, *i.e.*, $\log \gamma_2'' = 0$

$$\therefore \ Lt.N_2'' \rightarrow 0, \quad -\left[\frac{E}{0.059} + \log N_2''\right] = -\log a_2' \ \ldots (21.11)$$

One of the electrodes must have a very dilute amalgam of activity a_2' and its concentration (N_2') should be kept constant. The concentrations of the amalgam in the other electrode are varied and the corresponding values of e.m.f. (E) are to be measured. Now, the quantity $-(E/0.059 + \log N_2'')$ is plotted against N_2'' and the curve (almost linear) is extrapolated to $N_2'' = 0$, (Fig. 21*d*). The intercept gives the value of $-\log a_2'$. Putting this value in eqn. (21.10), the activity coefficients γ_2'' for different amalgams (having different N_2'') can be easily calculated and hence the values of a_2''.

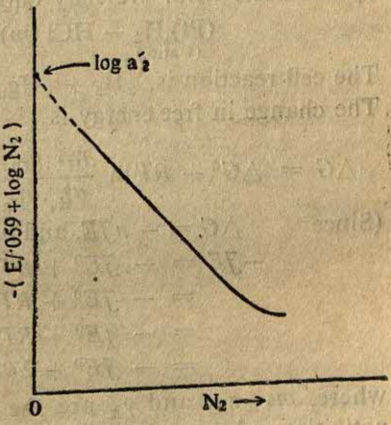


Fig. 21*d*.
Graphical determination of a_2'

Example : A thallium amalgam cell,

$\text{Hg-Tl}_x(N_2'' = 0.1680)$ – Tl-salt solution – $\text{Tl}_y\text{-Hg}(N_2' = 0.00326)$

$(a_2'' = ?)$ $(a_2' = 0.003396)$

has an e.m.f. of −0.1356 volts at 20°C; calculate the activity a_2'' of thallium in the amalgam of the concentrated electrode.

$$\log \gamma_2'' = -\frac{E}{0.058} - \log N_2'' + \log a_2'$$

$$= \frac{0.1356}{0.058} - \log 0.168 + \log 0.003396 = 0.6361$$

or $\gamma_2'' = 4.321$

Hence $a_2'' = N_2'' \times \gamma_2'' = 0.1680 \times 4.321 = 0.7259$

(*ii*) *Electrolytes* : In determining the mean activity of an electrolyte, it is necessary to construct a cell in which the two electrodes would be reversible with respect to the two ions produced by the dissociation of the electrolyte. So, to measure the mean activity of the electrolyte MA, a cell of the type,

$$\text{M}-\underset{(\text{molality}, m)}{\text{MA in solution}}-\text{A}$$

is to be taken, one electrode is reversible with respect to the cation M^+ and another to the anion A^-.

Suppose we have to determine the mean activity coefficient of hydrochloric acid. We may choose the cell,

$$(\text{Pt})\,\underset{(1\text{ atm.})}{H_2} - HCl\,(m) - Hg_2Cl_2 - Hg$$

The cell reaction is, $\frac{1}{2}H_2 + \frac{1}{2}Hg_2Cl_2 = H^+ + Cl^- + Hg$

The change in free energy is

$$\triangle G = \triangle G^0 + RT \ln \frac{a_{H^+}.a_{Cl^-}.a_{Hg}}{a^{\frac{1}{2}}_{H_2}.a^{\frac{1}{2}}_{Hg_2Cl_2}} = \triangle G^0 + RT \ln (a_{H^+}.a_{Cl^-})$$

(Since $\triangle G = -nJE$, and $n = 1$, $a_{Hg} = a_{Hg_2Cl_2} = a_{H_2} = 1$)

$$\begin{aligned} -JE &= -JE^0 + RT \ln a_{H^+}.a_{Cl^-} \\ &= -JE^0 + RT \ln a^2_{\pm} \\ &= -JE^0 + RT \ln (m_{\pm}\gamma_{\pm})^2 \\ &= -JE^0 + 2RT \ln m_{\pm} + 2RT \ln \gamma_{\pm} \end{aligned}$$

where, $m_{\pm}$, $a_{\pm}$, and $\gamma_{\pm}$ are the corresponding mean values. The activities and the activity coefficients are taken on molality basis.

Remembering, for binary strong electrolyte hydrochloric acid, $m_{\pm} = m$, (molality of the given acid solution), we have

$$\frac{2RT}{J} \ln \gamma_{\pm} = E^0 - \left(E + \frac{2RT}{J} \ln m\right)$$

$$\therefore \text{ At } 25°\text{C}, \quad \log \gamma_{\pm} = \frac{E^0}{0.118} - \left(\frac{E}{0.118} + \log m\right) \quad \ldots (21.12)$$

E is measured and m is known. Therefore, $\gamma_\pm$ can be found out only if E^0 could be evaluated. It is, however, known that at infinite dilution $\gamma^\pm \to 1$, or $\log \gamma_\pm \to 0$. Hence, at infinite dilution,

$$I\,t.m \to 0,\ E^0 = E + 0.118 \log m$$

In practice, e.m.f. (E) of the cell is measured using different dilute solutions of hydrochloric acid. $E + 0.118 \log m$ is then plotted against some function of the molality of the solution (say, against $\sqrt{m}$) and the curve is extrapolated to zero molality ($m = 0$) when E^0 is obtained. Substitution of E^0 in equation (21.12) gives the value of the mean activity coefficient ($\gamma_\pm$) of the hydrochloric acid solution.

According to Debye's limiting law, $\log \gamma_\pm = -a\sqrt{m}$. This means that if the terms in the paranthesis of right-hand side be plotted against $\sqrt{m}$, the graph is linear, which facilitates easy extrapolation.

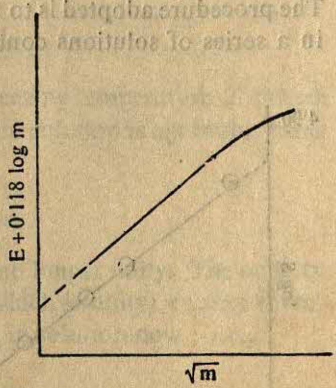


Fig. 21e. Determination of E°

21.4. Activity coefficients from solubilities

The measurment of solubilities is often utilised to ascertain the activity coefficients, and hence activity, of sparingly soluble electrolytes. The equilibrium in the dissociation of a slightly soluble salt $B_{n+}A_{n-}$ in a saturated solution is given by

$$B_{n+}A_{n-} \rightleftharpoons n_+B^+ + n_-A^-$$

The activity product, $L_a = a_{B+}^{n+}.a_{A-}^{n-}$

where a_{B+} and a_{A-} are the activities of the positive and negative ions respectively. Introducing concentration in terms of molality, and putting $n_+ + n_- = \nu$,

$$L_a = (m_{B_+}\gamma_+)^{n+}.(m_{A^-}\gamma_-)^{n^-} = (m_\pm.\gamma_\pm)^\nu$$

Since mean ionic molality $m_\pm = s$, solubility of the salt in molal units,

$$L_a = s^\nu.(\gamma_\pm)^\nu; \qquad (\gamma_\pm = \text{mean activity coefficient})$$

or

$$\therefore\ \gamma_\pm = L_a^{\frac{1}{\nu}}/s$$

It means that if the solubility of the sparingly soluble salt and the activity product be known, its mean activity coefficient can be evaluated. To illustrate, with a simple uni-univalent electrolyte say silver chloride, where $\nu = n_+ + n_- = 2$, we have in a saturated solution of AgCl,

$$\gamma_\pm = \sqrt{L_a}/s \qquad \ldots (21.13)$$

The procedure adopted is to measure the solubility of silver chloride in a series of solutions containing decreasing concentrations of an added electrolyte, say $NaNO_3$. The solubilities may then be plotted against the salt concentrations and then extrapolated to zero concentration. At zero concentration, $\gamma_\pm \rightarrow 1$, so,

$$L_a^{\frac{1}{2}} = s_0 \text{ (from the graph)}$$

$$\therefore \; \gamma_\pm = s_0/s$$

where s_0 is the solubility in the hypothetical zero ionic strength. The result of extrapolation becomes very accurate when the logarithm of the solubility is plotted against the square root of the ionic strength. In such a case the curve being linear, accurate extrapolation is possible, as in Fig. 21*f*.

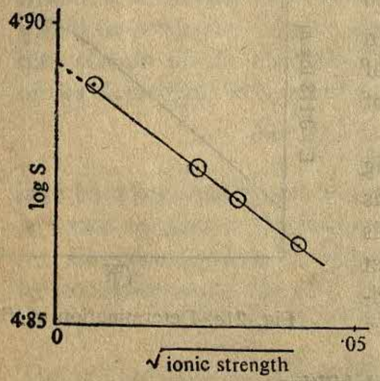


Fig. 21*f*. Solubility of AgCl and ionic strength

21.5. The cryoscopic method

It is possible to utilise the measurement of the freezing point depression for determining the activity or the activity coefficient and the method is capable of yielding results of high precision.

Consider an aqueous solution containing n_1 mols of water and n_2 mols of the solute. We shall use suffix 1, 2 and s for the liquid solvent, solute and the solid state of the solvent (ice) respectively. Let T_0 and T denote the freezing points of the pure solvent and the solution. (It is presumed that pure solvent only crystallises from the solution at the freezing point).

At the freezing point of the pure solvent T_0, the fugacity of water must be the same in both the solid and the liquid phase.

$$\mathrm{f}_{\text{ice}} = \mathrm{f}_{\text{water}}$$

Since each phase is in the pure (standard) state, hence the activity in each case is unity.

$$\therefore \qquad a_{\text{ice}} = a_{\text{water}} = 1$$

When we take the solution at its freezing temperature T (which is lower than T_0) the fugacity of water in solution is again the same as that of ice separating.

$$\mathrm{f}_{\text{ice}} = \mathrm{f}_{\text{water in solution}}$$

But the activity of water in solution is no longer unity. The activity of ice measured in its own standard (which is unity) cannot therefore be equal to the activity of water a_1 in solution now ; *i.e.*, .

$$a_{\text{ice}} \neq a_{\text{water in solution}}$$

If we accept the pure super-cooled liquid at the specified temperature (T) as the standard to measure all activities of the solvent including its solid state, then

$$a_s = a_{\text{water in solution}} \qquad \text{or} \quad a_s = a_1$$

(It may be remembered that a_s, the activity of the solid ice in equilibrium with solution is different from the previous a_{ice} as the standard state is different.)

For the process of freezing at any temperature T,

$$H_2O_{\text{liquid}} \rightarrow H_2O_{\text{ice}},$$

the change in free energy would be,

$$\triangle G = RT \ln \frac{\mathrm{f}_{\text{ice}}}{\mathrm{f}_{\text{pure waer}}} = RT \ln \frac{\mathrm{f}_{\text{ice}}}{\mathrm{f}^{0}_{\text{(standard)}}} = RT \ln a_s = RT \ln a_1$$

$$\therefore \qquad \frac{\triangle G}{T} = R \ln a_1$$

$$\text{or} \qquad \left(\frac{\partial(\triangle G/T)}{\partial T}\right)_P = R \left(\frac{\partial \ln a_1}{\partial T}\right)_P$$

From Gibbs-Helmholtz relation (equation 6.26),

$$\left(\frac{\partial(\triangle G/T)}{\partial T}\right)_P = -\frac{\triangle H}{RT^2}$$

$$\therefore \quad \left(\frac{\partial \ln a_1}{\partial T}\right)_P = -\frac{\triangle H}{RT^2} = \frac{L}{RT^2} \qquad \ldots (21.14)$$

where L is the molar latent heat of fusion of ice, and $-\triangle H = L$.

The latent heat L varies with temperature and we can use Kirchhoff's equation for the same,

$$\left(\frac{dL}{dT}\right)_P = \triangle C_P = (C_P)_l - (C_P)_s$$

or

$$L = L_0 + \triangle C_P(T - T_0)$$

assuming $\triangle C_P$ to remain constant during the small range of temperature variation. If the lowering of freezing temperature $(T_0 - T)$ is replaced by θ, then the equation (21.14) becomes

$$\frac{d \ln a_1}{dT} = \frac{L_0 - \theta \triangle C_P}{RT^2} \qquad \ldots (21.15)$$

$L_0 =$ molar latent-heat of fusion of the solid at T_0.
Now $T = T_0 - \theta$; *i.e.*, $dT = -d\theta$

$$\therefore \quad \frac{1}{T^2} = \frac{1}{(T_0-\theta)^2} = \frac{1}{T_0^2}\left[1 - \frac{\theta}{T_0}\right]^{-2} = \frac{1}{T_0^2}\left[1 + \frac{2\theta}{T_0} + \frac{3\theta^2}{T_0^2} + \ldots\right]$$

Substituting in equation (20.15)

$$-d \ln a_1 = \frac{(L_0 - \theta \triangle C_P)}{R(T_0-\theta)^2} d\theta$$

$$= \frac{(L_0 - \theta \triangle C_P)}{RT_0^2}\left(1 + \frac{2\theta}{T_0} + \frac{3\theta^2}{T_0^2} + \ldots\right) d\theta$$

$$= \left[\frac{L_0}{RT_0^2} + \frac{1}{RT_0^2}\left\{\left(\frac{2L_0}{T_0} - \triangle C_P\right)\theta\right.\right.$$

$$\left.\left. + \left(\frac{3L_0}{T_0^2} - \frac{2\triangle C_P}{T_0}\right)\theta^2 + \ldots\right\}\right] d\theta \qquad \ldots (21.16)$$

Integrating between a_1(for pure solvent) $= 1$, to a_1 the activity in the solution, when the limits of $\theta = 0$, to $\theta = \theta$,

$$-\ln a_1 = \frac{L_0 \theta}{RT_0^2} + \frac{\theta^2}{RT_0^2}\left(\frac{L_0}{T_0} - \frac{\triangle C_P}{2}\right) + \ldots \qquad \ldots (21.17)$$

In the case of aqueous solutions, $L_0 = 1438$ cal/mole and $\triangle C_p = 9$ calories, then

$$-2.303 \log a_1 = \frac{1438}{2\times273^2}\,\theta + \left(\frac{1438}{273} - \frac{9}{2}\right)\frac{\theta^2}{2\times273^2}$$

or $$\log a_1 = -4.2\times10^{-3}\theta - 2.2\times10^{-6}\theta^2$$

The freezing point depression θ is exprimentally measured with sufficient accuracy and the activity of the solvent is evaluated.

For the determination of the activity of the solute, the value of the activity of the solvent ascertained by equation (20.17) may be employed as in Sec. (21.2). The relation between the activities of the solute and the solvent is given by

$$d\ln a_2 = -\frac{N_1}{N_2}\,d\ln a_1 = -\frac{n_1}{n_2}\,d\ln a_1$$

If the solution taken be m molal (*i.e.*, m gm-mole of the solute be present in 1000 gm of the solvent), then $n_2 = m$, and

$$n_1 = \frac{1000}{M_1},\ \text{where } M_1 = \text{molecular weight of the solvent.}$$

$$\therefore\quad d\ln a_2 = -\frac{1000}{mM_1}\,d\ln a_1 \qquad \ldots (21.18)$$

$$= \frac{1000}{mM_1}\left[\frac{L_0}{RT_0^2} + \left(\frac{2L_0}{T_0} - \triangle C_P\right)\frac{\theta}{RT_0^2} + \ldots\right]d\theta,$$

by substitution from (21.16).
Now, the molal freezing-point constant, from Sec. (16.5) is

$$k_f = \frac{RT_0^2}{1000\times l} = \frac{RT_0^2.M_1}{1000\times L_0}, \qquad [\because\ l\times M_1 = L_0]$$

Substituting this in the relation above,

$$d\ln a_2 = \frac{1}{k_f m}\,d\theta + \frac{1}{k_f m}\left(\frac{2L_0}{T_0} - \triangle C_P\right)\theta d\theta + \ldots$$

Putting $$\frac{1}{k_f}\left(\frac{2L_0}{T_0} - \triangle C_P\right) = \phi \text{ (constant)},$$

$$d\ln a_2 = \frac{1}{k_f m}\,d\theta + \phi\frac{\theta}{m}\,d\theta, \qquad \ldots (21.19)$$

neglecting higher powers of θ.

From Gibbs-Helmholtz relation (equation 6.26),

$$\left(\frac{\partial(\triangle G/T)}{\partial T}\right)_P = -\frac{\triangle H}{RT^2}$$

$$\therefore \quad \left(\frac{\partial \ln a_1}{\partial T}\right)_P = -\frac{\triangle H}{RT^2} = \frac{L}{RT^2} \qquad \ldots (21.14)$$

where L is the molar latent heat of fusion of ice, and $-\triangle H = L$.

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$L_0 =$ molar latent-heat of fusion of the solid at T_0.

Now $T = T_0 - \theta$; *i.e.*, $dT = -d\theta$

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Substituting in equation (20.15)

$$-d \ln a_1 = \frac{(L_0 - \theta \triangle C_P)}{R(T_0 - \theta)^2} d\theta$$

$$= \frac{(L_0 - \theta \triangle C_P)}{RT_0^2}\left(1 + \frac{2\theta}{T_0} + \frac{3\theta^2}{T_0^2} + \ldots\right) d\theta$$

$$= \left[\frac{L_0}{RT_0^2} + \frac{1}{RT_0^2}\left\{\left(\frac{2L_0}{T_0} - \triangle C_P\right)\theta\right.\right.$$

$$\left.\left. + \left(\frac{3L_0}{T_0^2} - \frac{2\triangle C_P}{T_0}\right)\theta^2 + \ldots\right\}\right] d\theta \qquad \ldots (21.16)$$

Integrating between a_1(for pure solvent) $= 1$, to a_1 the activity in the solution, when the limits of $\theta = 0$, to $\theta = \theta$,

$$-\ln a_1 = \frac{L_0 \theta}{RT_0^2} + \frac{\theta^2}{RT_0^2}\left(\frac{L_0}{T_0} - \frac{\triangle C_P}{2}\right) + \ldots \qquad \ldots (21.17)$$

In the case of aqueous solutions, $L_0 = 1438$ cal/mole and $\triangle C_p = 9$ calories, then

$$-2.303 \log a_1 = \frac{1438}{2\times273^2}\,\theta + \left(\frac{1438}{273} - \frac{9}{2}\right)\frac{\theta^2}{2\times273^2}$$

or
$$\log a_1 = -4.2\times10^{-3}\theta - 2.2\times10^{-6}\theta^2$$

The freezing point depression θ is exprimentally measured with sufficient accuracy and the activity of the solvent is evaluated.

For the determination of the activity of the solute, the value of the activity of the solvent ascertained by equation (20.17) may be employed as in Sec. (21.2). The relation between the activities of the solute and the solvent is given by

$$d \ln a_2 = -\frac{N_1}{N_2}\, d \ln a_1 = -\frac{n_1}{n_2}\, d \ln a_1$$

If the solution taken be m molal (*i.e.*, m gm-mole of the solute be present in 1000 gm of the solvent), then $n_2 = m$, and

$$n_1 = \frac{1000}{M_1}, \text{ where } M_1 = \text{molecular weight of the solvent.}$$

$$\therefore\quad d \ln a_2 = -\frac{1000}{mM_1}\, d \ln a_1 \qquad \ldots (21.18)$$

$$= \frac{1000}{mM_1}\left[\frac{L_0}{RT_0^2} + \left(\frac{2L_0}{T_0} - \triangle C_P\right)\frac{\theta}{RT_0^2} + \ldots\right] d\theta,$$

by substitution from (21.16).
Now, the molal freezing-point constant, from Sec. (16.5) is

$$k_f = \frac{RT_0^2}{1000\times l} = \frac{RT_0^2.M_1}{1000\times L_0}, \qquad [\because l\times M_1 = L_0]$$

Substituting this in the relation above,

$$d \ln a_2 = \frac{1}{k_f m}\, d\theta + \frac{1}{k_f m}\left(\frac{2L_0}{T_0} - \triangle C_P\right)\theta d\theta + \ldots$$

Putting
$$\frac{1}{k_f}\left(\frac{2L_0}{T_0} - \triangle C_P\right) = \phi \text{ (constant)},$$

$$d \ln a_2 = \frac{1}{k_f m}\, d\theta + \phi\frac{\theta}{m}\, d\theta, \qquad \ldots (21.19)$$

neglecting higher powers of θ.

In the case of the solute being an electrolyte producing ions numbering ν, we know,

$$a_2 = a_\pm^\nu = a_+^{n+}.a_-^{n-}$$

Then, $$\nu\, d \ln a_\pm = \frac{1}{k_f m}\, d\theta + \phi\, \frac{\theta}{m}\, d\theta$$

or $$d \ln a_\pm = \frac{1}{\nu k_f m}\, d\theta + \phi\, \frac{\theta}{\nu m}\, d\theta \qquad \ldots (21.20)$$

For simplifying the process of integration of this equation, Lewis and Randall introduced a very convenient j-function. j is defined by the relation,

$$j = 1 - \frac{\theta}{\nu k_f m}.$$

In very dilute solution, *i.e.*, as $m \rightarrow 0$, the observed depression of freezing temperature $\theta \rightarrow \nu k_f m$.

$$\therefore \qquad Lt. m \rightarrow 0; \;\; j \rightarrow 0$$

Further, $$dj = \frac{\theta}{\nu k_f} . \frac{dm}{m^2} - \frac{d\theta}{\nu k_f m}$$

$$= (1 - j)\, \frac{dm}{m} - \frac{d\theta}{\nu k_f m}$$

or $$\frac{d\theta}{\nu k_f m} = (1 - j)\, \frac{dm}{m} - dj \qquad \ldots (21.21)$$

With substitution from (21.21), the equation (21.20) takes the form,

$$d \ln a_\pm = (1 - j)\, \frac{dm}{m} - dj + \phi\, \frac{\theta}{\nu m}\, d\theta$$

$$= (1 - j)\, d \ln m - dj + \phi\, \frac{\theta}{\nu m}\, d\theta \ldots (21.22)$$

or, $d \ln \gamma_\pm + d \ln m_\pm = (1-j)\, d \ln m - dj + \phi\, \dfrac{\theta}{\nu m}\, d\theta$

[But $(m_\pm)^\nu = m_+^{n_+} . m_-^{n_-} = (m.n_+)^{n_+}(m.n_-)^{n_-} = m^\nu(n_+^{n_+} . n_-^{n_-})$]

i.e., $\ln m_\pm = \ln m + \dfrac{1}{\nu} \ln (n_+^{n_+} . n_-^{n_-}) = \ln m + \text{const.}$

or $\qquad d \ln m_\pm = d \ln m$]

Hence, $d \ln \gamma_{\pm} = -d \ln m + (1-j)\, d \ln m - dj + \phi \dfrac{\theta}{\nu m}\, d\theta$

$$= -j \frac{dm}{m} - dj + \phi \frac{\theta}{\nu m}\, d\theta$$

In dilute solutions as $m \to 0$, $\gamma_{\pm} \to 1$, or $\ln \gamma_{\pm} \to 0$

$$\therefore \quad \int_0^{\ln \gamma_{\pm}} d \ln \gamma_{\pm} = -\int_0^m j \frac{dm}{m} - j + \int_0^m \phi \frac{\theta}{\nu m}\, d\theta$$

$$\text{or} \quad \ln \gamma_{\pm} = -\int_0^m \frac{j}{m}\, dm - j + \int_0^m \frac{\phi}{\nu} \frac{\theta}{m}\, d\theta \qquad \ldots (21.23)$$

The integrals on the right-side are determined graphically. Two curves are plotted, (*i*) $\dfrac{j}{m}$ against m and (*ii*) $\dfrac{\theta}{m}$ against θ. The plots require the experimental determination of freezing point measurements at different concentrations, m. The areas under the curves would give the value of the two integrals. The activity coefficient of the solute is thus known.

The equation (21.23) is quite accurate for dilute solutions. But when the solutions are concentrated, the freezing points vary appreciably and the results cannot be referred to the same temperature. In such cases, a correction has to be made taking into consideration the differential heat of dilution.

It can be shown that the activity coefficient $\gamma^{\circ}_{\pm}$ referred to a standard temperature can be expressed as

$$ln\ \gamma^{\circ}_{\pm} = \ln \gamma_{\pm} - \frac{n_1}{\nu} \int \frac{1}{m}\, d \ln \frac{a_1^{\circ}}{a_1},$$

a_1° is the activity of the solvent at the reference temperature.

21.6. Activity coefficient from the Osmotic coefficient

In an ideal system, the chemical potential of the component having mole-fraction N_i is given by

$$\mu_i = \mu_i^{\circ} + RT \ln N_i$$

But when the system is non-ideal,

$$\mu_i = \mu_i^{\circ} + RT \ln N_i \gamma_i$$

where γ_i is the activity coefficient and is a measure of the deviation from ideality.

Bjerrum and Guggenheim, however, introduced the osmotic coefficient ϕ to denote the deviation from ideality by expressing the chemical potential in the form

$$\mu_i = \mu_i^\circ + \phi\, RT \ln N_i$$

The relation between the activity coefficient and the osmotic coefficient is then

$$\phi \ln N_i = \ln N_i\gamma_i$$

$$\left.\begin{aligned} \text{or} \qquad \phi - 1 &= \frac{\ln \gamma_i}{\ln N_i} \\ \textit{i.e.,} \qquad \phi &= 1 + \frac{\ln \gamma_i}{\ln N_i} \end{aligned}\right\} \qquad \ldots (21.24)$$

In highly dilute solutions, mol-fraction of the solvent N_1 approaches unity, and γ_1 also tends to unity, so that $\ln \gamma_1 \rightarrow 0$. The ratio $\frac{\ln \gamma_1}{\ln N_1}$ may give large values of $(\phi - 1)$ even in very dilute solutions and therefore ϕ is very sensitive to deviations from ideality.

Now, consider a binary solution (solute and solvent). From the Gibbs-Duhem relations, as shown in equation (21.4),

$$N_1 d \ln \gamma_1 + N_2 d \ln \gamma_2 = 0,$$

the suffix 1 is used for the sovent and 2 for the solute.

Since $\ln \gamma_1 = (1 - \phi) \ln \frac{1}{N_1}$, [from equation (21.24)]

$$N_1 d \left\{ (1 - \phi) \ln \frac{1}{N_1} \right\} + N_2 d \ln \gamma_2 = 0$$

or $$-N_1 \ln \frac{1}{N_1} d\phi - (1 - \phi)\, dN_1 + N_2 d \ln \gamma_2 = 0$$

Now $dN_1 = -dN_2$, $\therefore\ N_1 \ln N_1 d\phi + (1 - \phi) dN_2 + N_2 d \ln \gamma_2 = 0$

or $(1 - N_2) \ln (1 - N_2)\, d\phi + (1 - \phi) dN_2 + N_2 d \ln \gamma_2 = 0$

In very dilute solutions, N_2 is very small, *i.e.*, $1 - N_2 \approx 1$

$$\therefore \qquad -d\phi + \frac{(1 - \phi) dN_2}{N_2} + d \ln \gamma_2 = 0$$

or $$d \ln \gamma_2 = d\phi - (1 - \phi)\, d \ln N_2$$

Again N_2 is proportional to molality m_2, *i.e.*, $d \ln N_2 = d \ln m_2$

$$\therefore \qquad d \ln \gamma_2 = d\phi - (1 - \phi)\, d \ln m_2 \qquad \ldots (21.25)$$

At infinite dilution, when $m_2 \rightarrow 0$, we know ϕ tends to unity and also $\gamma_2 \rightarrow 1$. Hence on integration of equation (21.25), between the limits corresponding to the given solution and that at infinite dilution, we have

$$\int_{\gamma_2 = \gamma_2}^{\gamma_2 = 1} d \ln \gamma_2 = \int_{\phi}^{1} d\phi - \int_{m_2}^{0} (1 - \phi)\, d \ln m_2$$

$$\text{or,} \qquad -\ln \gamma_2 = (1-\phi) + \int_{0}^{m_2} (1-\phi)\, d \ln m_2 \ldots \qquad \ldots (21.26)$$

$$= (1-\phi) + \int_{0}^{\sqrt{m_2}} \frac{1-\phi}{\sqrt{m_2}}\, d(m_2)^{\frac{1}{2}} \qquad \ldots (21.26a)$$

In the event of the solute being an electrolyte, the equation may be modified as

$$-\ln \gamma_{\pm} = (1-\phi) + 2 \int_{0}^{\sqrt{m_2}} \frac{1-\phi}{\sqrt{m}} . dm^{\frac{1}{2}} ,$$

($\gamma_{\pm}$ = mean ionic activity coefficient)

To evalute γ_2, it is necessary to determine ϕ and also the value of the integral on the right-hand side. The osmotic coefficient ϕ is determined from vapour-pressure measurements. For the solvent component in dilute solutions,

$$\ln a_1 = \mu_1 - \mu_1{}^0$$

But $\qquad \phi RT \ln N_1 = \mu_1 - \mu_1{}^0$

Again, $\qquad a_1 = \frac{\mathbf{f}_1}{\mathbf{f}_1{}^0} \approx \frac{P_1}{P_1{}^0}$

Hence $\qquad \ln \frac{P_1}{P_1{}^0} = \phi \, RT \ln N_1$

i.e., ϕ is known from the measurement of vapour pressures.

The osmotic coefficient (ϕ), which is practically equal to the ratio of the actual to the ideal osmotic pressure of the given solution, can also be shown to be the ratio of the observed freezing point depression to the ideal value ($k_f m$).

The integrand in equation (21.26*a*) is determined graphically, by plotting $\frac{1-\phi}{\sqrt{m_2}}$ against $\sqrt{m_2}$ and measuring the area under the curve. We can thus determine γ_2.

21.7. Isopiestic method

By comparing the vapour pressures of the solutions of two electrolyte solutes, it is possible to evaluate the mean activity of one of the solute in a given solution provided the activities of the other at different concentrations be known. If two solutions of the two electrolytes in the same solvent be kept in an evacuated space, the solvent from the solution having higher vapour pressure and fugacity will distil over into the solution with lower vapour pressure until both have the same vapour pressure and equilibrium is established. Such solutions whose concentrations may be different, but have the same vapour pressure are called *isopiestic*. In such circumstances, the solvent in the two solutions has identical activity, a_1. Let us use the following symbols for the two solutions of A and B.

	Solute A	Solute B
Activity	a_A	a_B
molality	m_A	m_B
no. of ions per molecule	ν_A	ν_B
mean activity	$a_{A_\pm}$	$a_{B_\pm}$

Let us also suppose A to be the electrolyte whose activities at different concentrations are known and we are required to find out the activity of B in solution. We also know $a_B = a_{B\pm}^{\nu_B}$. The suffix 1 is always used for the solvent.

From Gibbs-Duhem relation, for the given solution of B,

$$-d\ln a_1 = \frac{n_B}{n_1}d\ln a_B = \frac{m_B}{1000/M_1}d\ln a_B$$

$$= \frac{\nu_B m_B}{1000/M_1}d\ln a_{B_\pm} \qquad \ldots \text{(I)}$$

Similarly, for the isopiestic solution of A,

$$-d\ln a_1 = \frac{\nu_A m_A}{1000/M_1}d\ln a_{A_\pm} \qquad \ldots \text{(II)}$$

Equating I and II ; and assuming $\nu_A = \nu_B$,

$$m_A\, d\ln a_{A_\pm} = m_B\, d\ln a_{B_\pm}$$

Introducing the respective activity coefficients,

$$m_A d\ln m_A\gamma_{A_\pm} = m_B\, d\ln m_B\gamma_{B_\pm}$$

$$d\ln\gamma_{B_\pm} = \frac{m_A}{m_B}\, d\ln m_A\gamma_{A_\pm} - d\ln m_B$$

$$= \frac{m_A}{m_B}\, d\ln m_A\gamma_{A_\pm} - d\ln m_B + (d\ln m_A + d\ln\gamma_{A\pm} - d\ln m_A\gamma_{A_\pm})$$

$$= d\ln\gamma_{A_\pm} + d\ln\frac{m_A}{m_B} + \left(\frac{m_A}{m_B} - 1\right) d\ln m_A\gamma_{A_\pm}$$

$$= d\ln\gamma_{A_\pm} + d\ln\phi' + (\phi' - 1)\, d\ln a_A$$

$$= d\ln\gamma_{A_\pm} + d\ln\phi' + (\phi' - 1)\frac{2}{\sqrt{a_A}}\left(da^{\frac{1}{2}}_A\right)$$

where $\phi' = \frac{m_A}{m_B}$, ratio of the molalities of the isopiestic solutions.

Integrating,

$$\ln\gamma_{B_\pm} = \ln\gamma_{A_\pm} + \ln\phi' + 2\int_0^{\sqrt{a}} (\phi'-1)\frac{1}{\sqrt{a_A}}\, da^{\frac{1}{2}}_A \qquad \ldots (21.27)$$

In very dilute solutions, as m_A and m_B tend to zero, both $\gamma_{B_\pm}$ and $\gamma_{A_\pm}$ tend to unity. The values of a_A and γ_A are known (determined separately by other methods). Now $(\phi' - 1)/\sqrt{a_A}$ is plotted against $\sqrt{a_A}$ and is extrapolated to zero. The area under the curve gives the magnitude of the integral on the right-hand side. The value of the desired activity coefficient can then be computed from the equation (21.27).

21.8. The Debye-Hückel theory

So far, we have considered the methods employed for the determination of activity or activity coefficient from the study of some property of the system. In the case of strong electrolytes, however, the activity coefficients can be calculated theoretically.

From the first decade of this century there was accumulating increasingly convincing evidence to show that the strong electrolytes are completely dissociated in solution. Yet the dilute solutions of strong electrolytes showed certain anomalies, *e.g.*, (*a*) inspite of complete ionisation with increasing dilution the conductivities of the solution increase in violation of the Arrhenius theory, (*b*) the measured activity coefficients of dilute ionic solutions deviate appreciably from unity showing departure from the validity of Henry's Law, etc. To explain these anomalies it is necessary to recognise the existence of interionic forces in the solution and only at infinite dilution these forces would vanish.

In a given concentration, the inter-ionic forces would give rise to additional free-energy (*G*) to the solution. Such free-energy would not exist if the particles were neutral and not charged ions. The additional free-energy acquired by the solution in a given concentration due to inter-ionic forces only can be measured by considering the electrical work involved in transferring the ions from a state of infinite dilution to the state of a given concentration.

In 1923, Debye and Hückel proposed a comparatively simple but elegant method to calculate the electrical work mentioned above. Their method is now commonly known as the Debye-Hückel theory of the strong electrolytes. The theory has certain limitations but for calculations in dilute solutions, it is generally applicable. The treatment however is not a truly thermodynamic one as it involves the consideration of individual ions and their properties. It is discussed here to confirm the results obtained from the thermodynamic treatment. The Debye-Hückel theory may broadly be derived in the following way.

Consider a solution containing per c.c. of the solvent n_1 ions of valency z_1, n_2 ions of valency z_2, n_3 ions of valency z_3, and so on. Let us fix our attention to one of these ions and this ion may be designated as the central ion. Due to its electrical character, in its immediate surroundings there would be a larger number of ions of the opposite sign than the number of ions with the same sign as that of the central ion. There is thus an ionic atmosphere of opposite sign surrounding the central ion. Every ion will have such ionic atmospheres. The charge-density of the ionic atmosphere is greatest in the immediate vicinity of the central ion and it gradually falls off with increasing distance.

Let ψ be the electric potential at a given point near the central ion. The electric potential is the measure of the work done to bring a unit charge to this point from an infinite distance where $\psi = 0$. The work done in bringing an ion of charge $z_i\epsilon$ to that point is $z_i\epsilon\psi$, where ϵ is the electronic charge and z_i is the valency of the ith kind of ion brought in. If we assume that the number of ions per c.c. at a great distance (where $\psi = 0$), is n_i, then by the Boltzmann distribution Law, the number of ions at the point where $\psi = \psi$, is given by $n_ie^{-z_i\Psi\epsilon/kT}$. The total charge carried to that point

$$= (z_i\epsilon)n_ie^{-z_i\epsilon\Psi/kT}. \quad (k = \text{Boltzmann constant.})$$

If we consider all the kinds of ions present in the system, the net charge per c.c. at the point, *i.e.*, charge-density ρ could be given by

$$\rho = n_1(z_1\epsilon)e^{-z_1\epsilon\Psi/kT} + n_2(z_2\epsilon)e^{-z_2\epsilon\Psi/kT} + \ldots + n_i(z_i\epsilon)e^{-z_i\epsilon\Psi/kT} + \ldots$$

$$= \Sigma n_iz_i\epsilon . e^{-z_i\epsilon\Psi/kT} \qquad \ldots (A)$$

The charge density is, however, related to the electric potential at the point by the Poisson equation,

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi\rho}{D} \qquad \ldots (B)$$

D, the dielectric constant of the medium.

Substituting (A) in (B), we have

$$\nabla^2\psi = -\frac{4\pi}{D}\Sigma n_iz_i\epsilon . e^{-z_i\epsilon\Psi/kT} \qquad \ldots (C)$$

In a dilute solution, assuming $z_i\epsilon\psi \leqslant kT$, we find

$$\nabla^2\psi = -\frac{4\pi}{D}\Sigma n_iz_i\epsilon\left(1 - \frac{z_i\epsilon\psi}{kT}\right)$$

$$= -\frac{4\pi}{D}\Sigma n_iz_i\epsilon + \frac{4\pi\epsilon^2}{DkT}\Sigma n_iz_i^2\psi$$

At a considerable distance, where $\psi = 0$, the total amount of positive and negative charges would be equal, *i.e.*,

$$\Sigma n_iz_i\epsilon = 0.$$

So, $$\nabla^2\psi = \frac{4\pi\epsilon^2}{DkT}\,\Sigma n_i z_i^2\psi \qquad \ldots \text{(D)}$$

or $$\nabla^2\psi = \kappa^2\psi \qquad \ldots \text{(E)}$$

where $$\kappa^2 = \frac{4\pi\epsilon^2}{DkT}\,\Sigma n_i z_i^2 \qquad \ldots \text{(F)}$$

Resolving equation (D), the solution of ψ in terms of distance r, from the central ion is given by

$$\psi = \frac{z\epsilon}{D}\cdot\frac{e^{-\kappa r}}{r} \qquad \ldots \text{(G)}$$

where $z\epsilon$ is the charge of the central ion.

$$\therefore \quad \psi = \frac{z\epsilon}{Dr} - \frac{z\epsilon}{D}\cdot\frac{\kappa}{1+\kappa r} \approx \frac{z\epsilon}{Dr} - \frac{z\epsilon\kappa}{D}, \qquad \ldots \text{H)}$$

assuming κr to be quite small compared to unity.

or $$\psi = \frac{z\epsilon}{Dr} - \frac{z\epsilon}{D.1/\kappa} \qquad \ldots \text{(I)}$$

From electrostatics, we know, the electric potential produced by the charge $z\epsilon$ of the central ion itself at a distance r from it would be given by

$$\psi_1 = \frac{z\epsilon}{Dr}$$

It may be remembered that the charge of the ionic atmosphere is equal in magnitude but opposite in sign to that of the central ion. If the charge of the ionic atmosphere be imagined to be concentrated at a point, distance $1/\kappa$, the electric potential produced by it at the ion would be $\psi_2 = -\dfrac{z\epsilon}{D.1/\kappa}$. The quantity $1/\kappa$ therefore is the measure of the *radius of the ionic atmosphere* and it would obviously depend upon the concentration of the solution. In equation (I) for the potential, the first term denotes the potential due to the charge of the ion itself and the second term is the potential due to the surrounding distribution of ions in the ionic atmosphere. In infinitely dilute solution, κ tends to zero or the potential due to the ionic atmosphere vanishes.

Let us imagine the central ion in uncharged (or neutral) state initially and let the charge $e = z\epsilon$ be imparted to it slowly in successive amounts of infinitesimal quantities. If the potential at the surface of the ion be ψ, the work done will be given by, [using equation (H)],

$$W = \int_0^{z\epsilon} \psi de = \int_0^{z\epsilon} \left(\frac{e}{Da} - \frac{e\kappa}{D} \right) de$$

where 'a' is the effective radius of the ion-particle or more appropriately, the closest approach between the ions. The work of charging the ion in infinite dilution and in a solution of a given concentration would be different. The work involved in the two cases are :

(*i*) In infinite dilution : $W_1 = \int_0^{z\epsilon} \left(\frac{e}{Da} - \frac{e\kappa}{D} \right) de$

$$= \int_0^{z\epsilon} \frac{e}{Da} de = \frac{z^2\epsilon^2}{2Da} \text{; (since } \kappa = 0)$$

(*ii*) In a given solution, $W_2 = \int_0^{z\epsilon} \left(\frac{e}{Da} - \frac{e\kappa}{D} \right) de$

$$= \frac{z^2\epsilon^2}{2Da} - \frac{z^2\epsilon^2}{2D}\kappa$$

The work done in transferring the charged ion from the solution in infinite dilution to that in given concentration,

$$\triangle W = W_2 - W_1 = - \frac{z^2\epsilon^2}{2D}\kappa \qquad \ldots \text{(J)}$$

If the solutions were ideal and if there were no electrical interionic forces, then the change in Gibbs potential in the transfer of the ion from a very dilute solution (concentration m_0 molal) to a given solution (concentration m molal) would be

$$\triangle G = \frac{RT}{N} \ln \frac{m}{m_0}, \text{ where } N \text{ is Avogadro number.}$$

In real solutions, the interionic forces are to be taken into account, and the Gibbs potential change would be

$$\triangle G = \frac{RT}{N} \ln \frac{m}{m_0} + \triangle W = \frac{RT}{N} \ln \frac{m}{m_0} - \frac{z^2\epsilon^2}{2D}\kappa \qquad \ldots \text{(K)}$$

Again for real solutions, introducing activity terms, we have

$$\triangle G = \frac{RT}{N} \ln \frac{a}{a_0} = \frac{RT}{N} \ln \frac{m\gamma}{m_0\gamma_0}, \text{ (γ-terms are activity coefficients)}$$

$$= \frac{RT}{N} \ln \frac{m\gamma}{m_0}, \quad \text{(in very dilute solutions $\gamma_0 \rightarrow 1$)}$$

$$= \frac{RT}{N} \ln \frac{m}{m_0} + \frac{RT}{N} \ln \gamma \qquad \ldots \text{(L)}$$

Comparing equation (K) and (L),

$$\frac{RT}{N} \ln \gamma = - \frac{z^2 \epsilon^2}{2D} \kappa$$

or

$$\ln \gamma = - \frac{z^2 \epsilon^2 N}{2DRT} \kappa \qquad \ldots \text{(M)}$$

In equation (F) it is seen, $\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \Sigma n_i z_i^2$ in which n_i is the number of the ith species of ion per c.c.

The molar concentration of the ion, $c_i = \frac{n_i}{N} 1000$

∴ The molal concentration of the ion, $m_i = \frac{n_i}{N} \frac{1000}{d}$

where d is the density of the solution, the same as that of the solvent, when the solution is dilute.

$$\therefore \qquad n_i = \frac{Nd}{1000} m_i$$

or

$$\Sigma n_i z_i^2 = \frac{Nd}{1000} \Sigma m_i z_i^2$$

The equation (M) may be rewritten,

$$\ln \gamma = - \frac{z^2 \epsilon^2 N}{2DRT} \kappa = - \frac{z^2 \epsilon^2 N}{2DRT} \left(\frac{4\pi\epsilon^2}{DkT} \frac{Nd}{1000} \Sigma m_i z_i^2 \right)^{\frac{1}{2}}$$

$$= - \frac{z^2 \epsilon^2 N}{2DRT} \left(\frac{4\pi\epsilon^2}{DkT} \frac{Nd}{1000} \right)^{\frac{1}{2}} \sqrt{\Sigma m_i z_i^2}$$

Since ionic strength (Sec. 10.19), $i = \frac{1}{2} \Sigma m_i z_i^2$,

we have, $\ln \gamma = - z^2 \left(\frac{\epsilon^2 N}{2DRT} \cdot \sqrt{\frac{4\pi\epsilon^2 Nd}{DkT 1000}} \right) \sqrt{2i}$

$$= - Bz^2 \sqrt{i} \qquad \ldots \text{(N)}$$

where $$B = \sqrt{2}\left(\frac{\epsilon^2 N}{2DRT}\sqrt{\frac{4\pi\epsilon^2 Nd}{DkT.1000}}\right)$$

$$= \frac{1}{(DT)^{3/2}}\left(\frac{\epsilon^2 N}{R}\sqrt{\frac{2\pi\epsilon^2 Nd}{k.1000}}\right) \qquad \ldots (P)$$

and is a constant when D and T are unaltered.

The equation (N) is then an expression for the activity coefficient γ, in terms of known measurable data.

The mean activity coefficient $\gamma_\pm$ of an electrolyte, say $A_{\nu+}\ B_{\nu-}$, is given by

$$\gamma_\pm^{\nu_+ + \nu_-} = \gamma_+^{\nu_+}.\gamma_-^{\nu_-}$$

or $$\ln \gamma_\pm = \frac{\nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-}{\nu_+ + \nu_-}$$

$$= \frac{\nu_+(-Bz_+^2\sqrt{i}) + \nu_-(-Bz_-^2\sqrt{i})}{\nu_+ + \nu_-}$$

$$= -B\sqrt{i}\left[\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\nu_+ + \nu_-}\right]$$

$$= -B\sqrt{i}.z_+ z_-, \quad (\text{Since } \nu_+ z_+ = \nu_- z_-)$$

$$\therefore \log_{10}\gamma_\pm = -\frac{B}{2.303}.\,|z_+|.|z_-|.\sqrt{i}$$

$$= -A.z_+ z_-.\sqrt{i} \qquad \ldots (Q)$$

where z_+ and z_- are the numerical values of the valences of the two ions of the electrolyte and $A = B/2.303$.

Using the values $\epsilon = 4.77 \times 10^{-10}$ e.s.u.; $N = 6.06 \times 10^{23}$; $k = 1.36 \times 10^{-16}$ ergs. at 25°C, in aqueous solutions, where $D = 78.54$, the value of A comes out to be 0.509.

$$\therefore \log_{10}\gamma_\pm = -0.509\, z_+ z_-.\sqrt{i} \approx -0.5 z_+.z_-.\sqrt{i} \qquad \ldots (R)$$

So, for different types of electrolytes, the mean activity coefficient would be,

	$\log_{10}\gamma_\pm$
Uni-univalent	$-0.5\sqrt{i}$
Uni-bivalent	$-1.0\sqrt{i}$
Uni-trivalent	$-1.5\sqrt{i}$
Bi-Bivalent	$-2.0\sqrt{i}$ etc.

For a single uni-univalent electrolyte in aqueous solution of molality m at 25°C. $\log_{10}\gamma_\pm = -0.5\sqrt{i} = -0.5\sqrt{m}$.

The equation (R) is often mentioned as the *Debye-Hückel Limiting law* and it gives the method for calculation of the activity coefficient of an electrolyte theoretically, at very dilute solutions. The law will be strictly valid as the concentration approaches zero, *i.e.*, at infinite dilution.

The validity of the Debye-Hückel theory for very dilute solutions ($i<0.01$) has been tested in two ways.

I. Since $\log \gamma_{\pm} = -Az_{+}.z_{-}.\sqrt{i}$, the plot of $-\log \gamma_{\pm}$ against $\sqrt{i}$ in dilute solutions would be linear and the slope of the line would give the value of $A.\ z_{+}.z_{-}$. This has been experimentally established. The activity coefficients of different cobaltammine salts were determined from solubility measurements in different ionic strengths (Bronsted and La Mer); the ionic strengths were varied by addition of salts like NaCl, KNO_3, $BaCl_2$ etc. The linear graphs obtained on plotting $\sqrt{i}$ vs. $-\log \gamma_{\pm}$ are shown in Fig (21*g*).

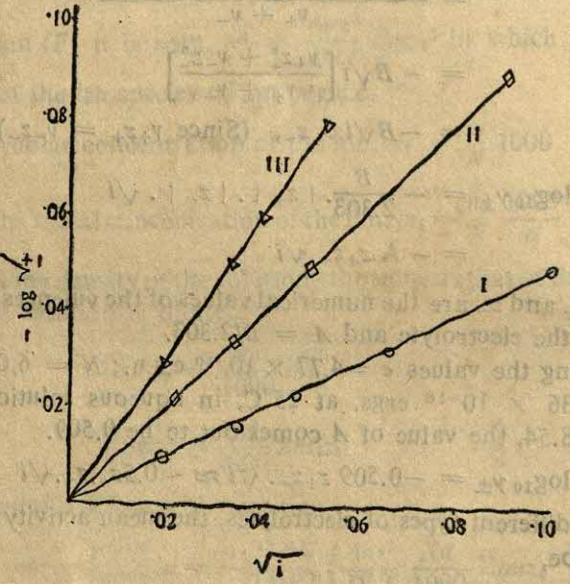


Fig. 21*g*. Activity coefficients vs. ionic strength.
I. Uni-univalent. II. Uni-bivalent. III. Uni-trivalent

The slopes obtained from the graphs corresponded to the calculated values of $Az_{+}z_{-}$. Moreover the same linearity was obtained irrespective of the nature of the salt added to vary the ionic strength, as expected from the theory.

II. It will be seen from equation (P) that for a given electrolyte the value of 'A' should be proportional to $\frac{1}{(DT)^{3/2}}$. Varying the temperature, the dielectric constant was widely altered. The slope of the line $\log \gamma_{\pm}$ vs. $\sqrt{i}$ at different temperatures has been determined to calculate A. The experimental results satisfy the theoretical requirements.

Apart from the fact that the limiting law enables us to calculate $\gamma_{\pm}$ in dilute solutions, where experimental values may not be available, the law is also used for various other purposes. For example, the thermodynamic equilibrium constant or the dissociation constant of a weak acid or base can be evaluated with the help of this law. In a weak acid, say HA, the true dissociation constant is given by,

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$

$$K_a = \frac{C_{H^+}.C_{A^-}}{C_{HA}} \cdot \frac{f_{H^+}.f_{A^-}}{f_{HA}} = K' f_{H^+}.f_{A^-}$$

where K' is the Ostwald's dissociation constant and f_{HA} is taken as unity.

$$\therefore \quad \log K' = \log K_a - \log f_{H^+} - \log f_{A^-}$$

Now, in a monobasic acid, $\log f_{H^+} = \log f_{A^-} = -A\sqrt{i}$

The ionic strentth, $i = \frac{1}{2}\,[C_{H^+} \times 1^2 + C_{A^-} \times 1^2]$

$$= \tfrac{1}{2}\,[\alpha c + \alpha c] = \alpha c,$$

α is the degree of dissociation.

$$\therefore \qquad \log K' = \log K_a + 2A\sqrt{\alpha c}.$$

By using the results of conductance measurements of solutions of different concentrations, αc and K' are known. The plot of $\log K'$ against $2A\sqrt{\alpha c}$ gives a straight line at very low concentrations (where the limiting law is valid). The intercept gives the value of $\log K_a$, from which K_a is known.

21.9. The Debye-Hückel theory in concentrated solution

It has been mentioned earlier that the Debye-Hückel theory would be valid only in very dilute solutions. In solutions of appreciable concentration, the extension of the limiting law has been made chiefly by Hückel and by Brönsted.

In deriving the Debye-Hückel equation two approximations have been made which are not permissible in more concentrated solutions. (*i*) The potential due to the ionic atmosphere ψ_2 has been approximated to $\frac{z\epsilon\kappa}{D}$ assuming κr to be very small, which is not so in case of concentrated solutions [see equation (H) Sec. 21.8]. (*ii*) The dielectric constant D of the medium has been assumed to be constant throughout the medium, which is not strictly true. In order to apply the Debye-Hückel equation to solutions of appreciable concentration, corrections have to be introduced on these two counts.

(*i*) The potential due to the ionic atmosphere should be

$$\psi^2 = -\frac{z\epsilon}{D}\cdot\frac{\kappa}{1+\kappa}$$

Using this expression for the ionic atmosphere and following the same treatment as before, it can be shown,

$$\log_{10}\gamma_{\pm} = -\frac{Az_+z_-\sqrt{i}}{1+a\kappa}$$

The value of κ is $\left(\frac{4\pi\epsilon^2}{DkT}\cdot\frac{Nd}{1000}\right)^{\frac{1}{2}}\sqrt{2i} = A_1\sqrt{i}$

where A_1 stands for $\sqrt{2}$ times the quantity within the paranthesis.

Hence $\log_{10}\gamma_{\pm} = -\frac{Az_+z_-\sqrt{i}}{1+aA_1\sqrt{i}}$ . . . (S)

This expression would always give smaller and smaller values for $\gamma_{\pm}$ with increasing concentrations. Experimental measurements however show that the activity coefficients first decrease with rise in the concentration and then increase after passing through a minimum value (Fig. 10*j*, Sec. 10.19). The expression, therefore, needs further correction.

(*ii*) The solvent molecules themselves are permanent dipoles and are influenced by the ions. The electric forces near the ions are quite strong. In consequence, the solvent molecules may compete with other ions in the formation of the ionic atmosphere. The orientation of the polar solvent molecules in the vicinity of the ions is likely to reduce the dielectric constant (D) appreciably. The dielectric constant therefore would vary from point to point. It has been presumed that this dielectric constant is a function of the concentration or the ionic strength. A complicated set of calculation shows that, to account for this variation of dielectric constant, an additional term proportional to the ionic strength has to be introduced in the equation (S), such that we can write,

$$\log_{10} \gamma_{\pm} = -\frac{Az_{+}z_{-}\sqrt{i}}{1 + aA_1\sqrt{i}} + A_2 i \qquad \ldots (T)$$

or

$$\log_{10} \gamma_{\pm} = -Az_{+}z_{-}\sqrt{i} + aA\,A_1 z_{+}z_{-} i + A_2 i$$

$$= -Az_{+}z_{-}\sqrt{i} + C.i$$

C = a constant for a given electrolyte.

This expression is in fair agreement with experimental results and is an extension of the Debye-Hückel law for the concentrated solutions.

Problems

1. The vap. pressures of pure mecury and a Thallium amalgam (mol-fraction of thallium, 0.16) are 20×10^{-4} and 15.2×10^{-4} mm. Calculate activity coefficent of mercury. **Ans.** $\gamma_{N_1} = 0.901$

2. In an aqueous solution of methyl alcohol, the partial pressures of the alcohol at different mol-fractions at 25°C are

N_2	P_2	N_2	P_2	N_2	P_2
0.0	0.0	0.08	15.10	0.66	85.7
0.02	3.85	0.10	26.00	0.80	104.6
0.04	7.67	0.20	35.8	1.00	126.0
0.06	11.70	0.40	59.6		

Calculate activity of alcohol at $N_2 = 0.7$.

[**Hints.** Plot P_2/N_2 against N_2. Find $P_2{}^*/N_2{}^*$ by extrapolation. Also determine P_2 at 0.7 N_2 from the graph] **Ans.** $a_2 = 0.468$

3. Show that the activity of the solvent, a_1 in a binary solution is given by

$$RT \ln a_1 = RT \ln \mathrm{f}_1/\mathrm{f}_1{}^0 = -\pi \overline{V}_1$$

where $\overline{V}_1$ partial molal volume of the solvent, π = osmotic pressure, f_1 and $\mathrm{f}_1{}^0$ are the fugacities of solvent in solution and in the pure state.

4. The solubility of $AgIO_3$ in different solutions of KNO_3 were recorded as,

Conc. KNO_3	0.00	0.00130	0.00325	0.00650	0.02140
Solubility, $AgIO_3$	0.00177	0.00182	0.00187	0.00191	0.00199

Find (*a*) the mean activity coefficient of $AgIO_3$ in pure water and (*b*) the solubility product of $AgIO_3$.

Ans. $\gamma_{\pm} = 0.985, L_s = 3 \times 10^{-8}$

5. The solubility product of silver bromate is 5.77×10^{-5} at 25°C. Show that its solubility in 0.01 *M* pot-bromate is 5.1×10^{-3} mole/litre. [Use Debye-Hückel Limiting Law.]

6. The e.m.f. of the cell

$$(\text{Pt})\ \text{H}_2-1\ \text{atm} \left| \begin{matrix} \text{HCl} \\ (\text{m} = 0.05391) \end{matrix} \right| \text{AgCl}-\text{Ag}$$

is 0.38222 volts. What is the mean activity coefficient of the HCl solution used? Given $E^{\circ}_{\text{Ag/AgCl}} = 0.2225$ volts.

Ans. $\gamma_{\pm} = 0.829$

7. The solubility of PbI_2 was found to be 6.8×10^{2} *g*/100 gm. Using Debye-Hückel Limiting Law, show that its activity product is 0.81×10^{8} mol^3/Kg^3.

8. The solubility of $BaSO_4$ in water is 9.57×10^{-6} molal and its heat of solution is 5970 cal/mole. The standard entropies of Ba^{++} and of $BaSO_4$ are 2.3 and 31.5 e.u./mole. Show that $S^{\circ}_{SO_4^{--}} = 3.2$ e.u.

CHAPTER 22

IRREVERSIBLE THERMODYNAMICS

We have, so far, developed the fundamentals of thermodynamics and applied them to study the properties and behaviour of systems which are supposed to exist in a state of equilibrium. It would be interesting if these principles be extended to systems in non-equilibrium states and in irreversible processes. The thermodynamics of irreversible processes, or as it is more often called non-equilibrium thermodynamics, is found to be very useful in examining coupled irreversible phenomena occurring simultaneously in a system. Most often such studies are made from the point of view of entropy-changes of the system.

22.1. Entropy Production

From classical thermodynamics, for a reversible process, the entropy-change is

$$dS = \left(\frac{\delta Q}{T}\right)_{rev}$$

And, from Clausius Inequality, we have, for an irreversible process,

$$dS > \left(\frac{\delta Q}{T}\right)_{irr}$$

We may rewrite this, at least for systems which are close to equilibrium, to restore equality, as

$$dS = \frac{\delta Q}{T} + d_iS \qquad \ldots \text{(A)}$$

The term d_iS would represent the extra entropy-change involved due to irreversibility. How this entropy is produced can be better understood by considering some examples.

(*i*) Suppose heat is conducted along a metallic wire *AB* from a reservoir at T_1 to a reservoir at T_2. T_1 is higher than T_2. Let the amount of heat transferred along the wire per unit time be I_Q. That is rate of flow of heat, (Fig. 22*a*),

$$\dot{Q} = \frac{dQ}{dt} = I_Q$$

The I_Q heat which enters the wire at A leaves the wire at B. The entropy of the wire does not change. On the other hand, the hot reservoir loses entropy I_Q/T_1 whereas the cold reservoir gains an entropy I_Q/T_2. per unit time. There is thus a net change in entropy of the universe, per unit time,

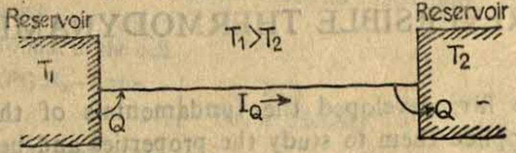


Fig. 22*a*. Heat flow

$$dS = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} = I_Q \frac{T_1 - T_2}{T_1 T_2}, \text{ which is positive.}$$

Now let us consider the wire (AB) only in this flow of heat. The entropy lost by hot reservoir at AI_Q/T_1 passes on to the wire. The entropy gained by the cold reservoir I_Q/T_2 comes out of the wire at B. Hence, the flow of entropy out of the wire at B, I_Q/T_2, is larger than the inflow of entropy A into the wire at A, I_Q/T_1. In a steady state, the wire does not change in coordinates. We have therefore to assume that during the irreversible flow of heat, an entropy $(I_Q/T_2 - I_Q/T_1)$ must have been produced in the wire per unit time in order to compensate for the extra flow of entropy into the cold reservoir.

The irreversible flow of heat thus leads to entropy production. The rate of entropy production is given by

$$\frac{d_i S}{dt} = I_Q \frac{T_1 - T_2}{T_1 T_2}$$

If the temperatures of the two reservoirs be quite close, such that $T_1 = T + \triangle T$ and $T_2 = T$, then the rate would be

$$\frac{d_i S}{dt} = I_Q \frac{\triangle T}{T^2}$$

or $$\frac{d_i S}{dt} = \frac{I_Q}{T} \cdot \frac{\triangle T}{T}$$

I_Q/T may be regarded as the rate of flow of entropy or entropy current and may be denoted by I_S. Then, the rate of production,

$$\dot{S} = \frac{d_i S}{dt} = I_S \cdot \frac{\triangle T}{T} \qquad \ldots \text{(B)}$$

(*ii*) Let us take a second example. Suppose two gases A and B mix at constant T and P. Imagine a mixing box $\bar{X}$ as in fig 22*b*, in which n_A moles of A and n_B moles of B enter per unit time. That is, the rates of inflow are $\dot{n}_A$ and $\dot{n}_B$. The moles of the mixture going out per unit time is $\dot{n}_m$. It is in effect a flow of matter.

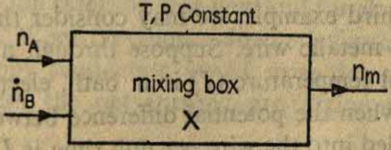


Fig. 22*b*. mixture of A and B

Let h_A, h_B be the molal enthalpies before mixing and h_m that of the mixture. Let $\bar{H}_A$, $\bar{H}_B$ denote the partial molal enthalpies of A and B in the mixture. Obviously,

$$\dot{n}_m h_m = \dot{n}_A \bar{H} + \dot{n}_B \bar{H}_B$$

Using the first Law of Thermodynamics, we can say,

$$\dot{q} + \dot{n}_A h_A + \dot{n}_B h_B = \dot{n}_m h_m = \dot{n}_A \bar{H}_A + \dot{n}_B \bar{H}_B$$

The process is isothermal, hence $\triangle S = 0$. Since the flow is irreversible, let $\frac{d_i S}{dt}$ denote the entropy production (if any) per unit time. Dividing the relation, written above, by T,

$$\frac{\dot{q}}{T} + \dot{n}_A \frac{h_A}{T} + \dot{n}_B \frac{h_B}{T} - \dot{n}_A \frac{\bar{H}_A}{T} - \dot{n}_B \frac{\bar{H}_B}{T} + \frac{d_i S}{dt} = 0$$

or
$$\frac{d_i S}{dt} = -\frac{\dot{q}}{T} - \dot{n}_A s_A - \dot{n}_B s_B - \dot{n}_A \bar{S}_A - \dot{n}_B \bar{S}_B$$

$$= -\frac{\dot{n}_A \bar{H}_A + \dot{n}_B \bar{H}_B - \dot{n}_A h_A - \dot{n}_B h_B}{T} - \dot{n}_A (s_A - \bar{S}_A)$$
$$- \dot{n}_B (s_B - \bar{S}_B)$$

$$= \dot{n}_A \left[\frac{h_A - \bar{H}_A}{T} - (s_A - \bar{S}_B)\right] + \dot{n}_B \left[\frac{h_B - \bar{H}_B}{T} - (s_B - \bar{S}_B)\right]$$

$$= \dot{n}_A \frac{\Delta\mu_A}{T} + \dot{n}_B \frac{\Delta\mu_B}{T}$$

$$\text{or} \quad \dot{S} = \frac{d_iS}{dt} = \sum_i \frac{\Delta\mu_i}{T}\dot{n}_i \qquad \ldots \text{(C)}$$

$\Delta\mu_i$ denoting the chemical potential changes.

This shows that there would be entropy production in the irreversible process of mixing.

(*iii*) In our third example, we may consider the flow of electricity through a metalic wire. Suppose through a metallic wire kept at a constant temperature (T) in a bath, electric current I is steadily passing when the potential difference between the ends is $\triangle\varepsilon$. The energy led into the wire per unit time is $I\triangle\varepsilon$. Since T is constant, this energy is dissipated as heat into the bath raising the entropy of the bath by $I\triangle\varepsilon/T$. per unit time. There was no entropy intake or flow into the wire. But $I\triangle\varepsilon/T$ amount of entropy passed out from the wire into the bath. In a steady state, this entropy which flows out to the bath must have been created or produced in the wire during the flow of electricity. Then, the entropy production per unit time during flow of electricity is

$$\dot{S} = \frac{d_iS}{dt} = I.\frac{\triangle\varepsilon}{T} \qquad \ldots \text{(D)}$$

If we look at equations (B), (C) & (D) above, we find that the expressions ($\dot{S}$) for rate of entropy-production are similar. In transfer of heat, the entropy flow I_s is multiplied by the temperature gradient ($\triangle T$), which causes the thermal flow. In the mixing of gases, likewise, the mass-flow is associated with the chemical potential gradient ($\triangle\mu$). Again in the transport of electricity, the current I (flow) is associated with the potential gradient ($\triangle\varepsilon$). In entropy production, the irreversible flows are always related to the associated thermodynamic potential gradients called thermodynamic forces.

A general expression for the rate of entropy production is given by

$$\dot{S} = \frac{d_iS}{dt} = \sum J_iX_i$$

where X_i represents the thermodynamic driving force and J_i represents the associated irreversible flow.

22.2. Coupled flows

When two different types of irreversible flows occur simultaneously in a system, that is in coupled flows, the rate of entropy production would depend upon both the flows. For example, if a small temperature difference $\triangle T$ be maintained at the two ends of a wire, there would be heat current I_Q (and hence I_s). Further, if a potential difference $\triangle \varepsilon$ exists between the ends of the wire, there would be an electric current I also. Hence, there would arise an irreversible coupled flow. In equations (B) and (D) above, the expressions for entropy production rates for heat-flow and for electric current have been developed. When the coupled flows exist in the wire simultaneously, the entropy production would arise due to both the flows. We may express the net entropy production rate as the sum of the two ;

$$\frac{d_iS}{dt} = I_s \frac{\triangle T}{T} + I \frac{\triangle \varepsilon}{T} \qquad \ldots (E)$$

But it is an experience that in absence of potential difference in the wire, the heat flow (I_Q) depends only on the temperature difference ($\triangle T$). But on imposition of potential difference ($\triangle \varepsilon$), the heat current changes as it depends upon both $\triangle T$ and $\triangle \varepsilon$.

Again at a constant temperature, the electric current I depends only on $\triangle \varepsilon$. But, in addition, if there exists a temperature difference ($\triangle T$), the electric current would depend upon both $\triangle \varepsilon$ and $\triangle T$. That is, in coupled processes, the two flows would react on one another.

If the system in which flows occur be not far removed from equilibrium, the flow-rates are considered to be linear functions of the forces $\triangle T$ and $\triangle \varepsilon$. So,

$$I_s = L_{11} \frac{\triangle T}{T} + L_{12} \frac{\triangle \varepsilon}{T} \qquad \ldots (F)$$

and

$$I = L_{21} \frac{\triangle T}{T} + L_{22} \frac{\triangle \varepsilon}{T} \qquad \ldots (G)$$

These are the well-known *Onsager equations*. The L-terms are called phenomenological coefficients. L_{11} and L_{22} are the coefficients for the thermal flow and for electrical flow only. The coefficients L_{12} and L_{21} arise due to the effect of interaction of the two forces. It was again Onsager who established that the latter two coefficients are identical, *i.e.*,

$$L_{12} = L_{21} \qquad \ldots (H)$$

This is called *Onsager's reciprocal condition*.

The equations (F) and (G) may now be considered under two specified conditions.

(*a*) Suppose the temperature is constant, ($\triangle T = 0$) then by dividing (F) by (G),

$$\left(\frac{I_s}{I}\right)_T = \frac{L_{12}}{L_{22}} = \epsilon \text{ (say)} \qquad \ldots \text{(I)}$$

ϵ is the ratio of the entropy current to the electric current at a constant temperature and is often mentioned as entropy transport parameter.

(*b*) In the absence of electric current, $I = 0$, we have from equation (G),

$$-\left(\frac{\triangle \varepsilon}{\triangle T}\right)_{I=0} = -\left(\frac{\partial \varepsilon}{\partial T}\right)_{I=0} = \frac{L_{21}}{L_{22}} = \frac{L_{12}}{L_{22}}$$

$$\text{hence} \quad -\left(\frac{\partial \varepsilon}{\partial T}\right)_{I=0} = \varepsilon \qquad \ldots \text{(J)}$$

$$\text{or} \quad \triangle \varepsilon = -\int_{T_2}^{T_1} \varepsilon dT \qquad \ldots \text{(K)}$$

Hence ϵ also represents the rate of change of potential with temperature at zero electric current. Hence, it is the *Seebeck Coefficient* (see Sec 20.5). The value of ϵ, course, depends upon the temperature and also the material.

22.3. Seebeck Effect

Consider a circuit as shown in fig. 22*c* Two dissimilar metals X and Y meet at junctions a and b. The two junctions are kept at two different temperatures T_1 and T_2; T_1 is higher than T_2. In consequence of difference in temperature at the two junctions a potential difference arises across the open circuit $d-c$, which can be

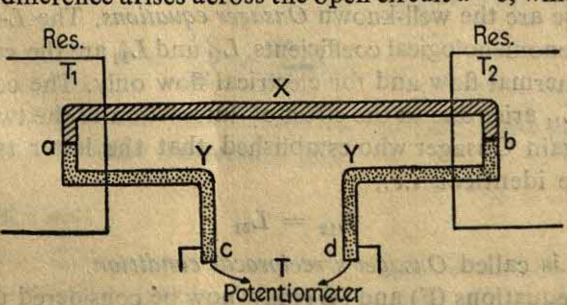


Fig. 22*c*. Seebeck Effect

measured against a balanced potentiometer. The potential difference $\triangle\varepsilon$ depends upon temperature difference $\triangle T (= T_1 - T_2)$ and on the nature of the metals X and Y.

If ε-terms denote the electric potentials at the different points, we may write,

$$\triangle\varepsilon = \varepsilon_d - \varepsilon_c = (\varepsilon_d - \varepsilon_b) + (\varepsilon_b - \varepsilon_a) + (\varepsilon_a - \varepsilon_c)$$

Using equation (K) above,

$$\triangle\varepsilon = -\int_{T_2}^{T} \epsilon_y dT - \int_{T_1}^{T_2} \epsilon_x dT - \int_{T}^{T_1} \epsilon_y dT$$

$$= \int_{T_2}^{T_1} \epsilon_x dT - \int_{T_2}^{T_1} \epsilon_Y dT$$

$$= \int_{T_2}^{T_1} (\epsilon_X - \epsilon_Y) dT$$

or $$\epsilon_x - \epsilon_y = \frac{d\varepsilon}{dT}$$

This difference $(\epsilon_x - \epsilon_y)$ gives the seebeck effect, for the materials X and Y.

or $$a_{xy} = \frac{d\varepsilon}{dT} \qquad \ldots \text{(L)}$$

22.4. Peltier Effect

Suppose two dissimilar metals X and Y are joined at the point J. The temperature is always maintained constant. An electric current (I) is allowed to pass through the metal bar. Suppose the junction

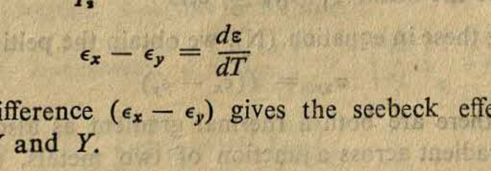


Fig. 22*d*. Peltier effect

has a resistance (r) and heat has to be removed to maintain constant temperature. If the system consisted of one metal, the heat escaping $(T = \text{constant})$ would have been I^2r per unit time. But in a system of dissimilar metals, the heat escaping would be different (say, I'_Q) from I^2r.

From the First Law,

$$I'_Q = (I^2r + I_{Q_x}) - I_{Q_y} \; ; \qquad (T = \text{constant}) \quad \ldots \text{(M)}$$

The peltier heat is defined as the additional heat to be removed at the junction other than the Joule heat I^2r. Let the peltier heat be denoted by I_{Q_π}.

Then $$I_{Q_\pi} = \pi_{xy} I = I'_Q - I^2{}_R$$

From equation (M), $$I_{Q_\pi} = \pi_{xy} I = I_{Q_x} - I_{Q_y} \quad \ldots \text{(N)}$$

We have seen in equation (I) above that

$$\epsilon_x = \left(\frac{I_{sx}}{I}\right)_T = \left(\frac{I_{Qx}}{IT}\right)_T$$

or $$I_{Qx} = \varepsilon_x IT$$

Similarly for the metal Y, $I_{Qy} = \varepsilon_y IT$

Substituting these in equation (N), we obtain the peltier cofficient,

$$\pi_{xy} = T(\epsilon_x - \epsilon_y) \quad \ldots \text{(P)}$$

When there are both a thermal gradient as also an electric potential gradient across a junction of two metals, the coupled reaction leads to Thomson effect, which has been discussed in Sec 20.7.

EXERCISES

[Use Tables for standard data where necessary.]

1. (*i*) At one atmosphere one c.c. of air when heated from 0°C to 100°C expands to a volume of 1.3671 c.c. Calculate the value of absolute zero using air-thermometer.

(*ii*) The limiting value of the ratio of the pressures of a gas between the ice-pt. and the steam-pt. is 1.36610. What is the ideal gas temperature at the steam-point?

(*iii*) Find out the numerical value of the conversion factor between work expressed in c.c.-atmospheres and in calories, when 1 cal = 4.186×10^7 ergs.

2. 340 gm of carbon dioxide are compressed from 100 litres to 10 litres at 60°C. Calculate the maximum work assuming the gas to be a van der Waals' one.

3. If β be the isothermal compressibility, show that,

(*a*) $\beta = 1/P$, for an ideal gas

(*b*) $\beta = \dfrac{1/P}{1 + bP/RT}$ for a gas obeying $P(v-b) = RT$

4. Derive the equation : $dv/v = \alpha dT - \beta dP$

5. One mole of nitrogen at N.T.P. is compressed isothermally and reversibly to one-half its original volume and then it is expanded adiabatically and reversibly to its original pressure. Calculate the net work done and show that the final temperature is 223°K.

6. The working substance of an engine operating a Carnot cycle is a gas obeying the equation of state, $P(v-b) = RT$. Show that its efficiency is the same as that with an ideal gas.

7. Water is heated but not allowed to expand. What temp.-rise is needed to produce 100 atm. **Ans.** 23.3°

8. Compare the efficiencies of two Carnot engines; one operates between 450°F and 70°F and the other between 1000°F and 70°F. **Ans.** $\eta_1 : \eta_2 = 21:32$

9. Show that for an ideal gas; $P\left(\frac{\partial C_p}{\partial P}\right)_V = T\left(\frac{\partial C_p}{\partial T}\right)_V$

10. If C_{p_1} and C_{p_2} be the heat-capacities of a van der Waals' gas at pressures P_1 and P_2, show that $C_{p_2} - C_{p_1} \approx 2a\,(P_2 - P_1)/RT^2$.

11. Suppose that f is the force needed to stretch a rubber strip of uniform cross section to length L. Show that for the strip,

(*a*) heat capacity, $C = \left(\frac{\partial U}{\partial T}\right)_L + \left[\left(\frac{\partial U}{\partial L}\right)_T - f\right]\left(\frac{\partial L}{\partial T}\right)$

(*b*) $\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L$

12. Show that (*a*) the ratio of the adiabatic and isothermal elasticity is the same as the ratio of heat-capacities at constant pressure and at constant volume.

(*b*) The difference is isothermal and adiabatic compressibilities is given by, $\beta_T - \beta_S = \alpha^2 vT/C_p$.

13. Prove :

(*a*) $\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)$

(*b*) $\left(\frac{\partial U}{\partial P}\right)_V = \frac{\beta}{\alpha} C_V$, (*c*) $\left(\frac{\partial U}{\partial V}\right)_P = C_V \frac{P}{R}$

(*d*) $\left(\frac{\partial H}{\partial V}\right)_T = -V^2\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial (T/V)}{\partial V}\right)_P$

(*e*) $\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_P$

14. If, in a Joule-Kelvin expansion, $(\partial v/\partial T)_P = v/T$, then there would be no temperature change.

15. In 'free expansion' of a gas, Joule-coefficient is given by $\eta = (\partial T/\partial v)_u$. Again, the Joule-Kelvin coefficient is expressed as $\mu = (\partial T/\partial P)_H$. Show that,

$$(a)\ \eta = \frac{1}{C_v}(P - \alpha T/\beta) \qquad (b)\ \mu = \frac{V}{C_p}(\alpha T - 1)$$

Also prove that $\eta[C_p - (\partial(PV)/\partial T] = C_p\mu + [\partial(PV)/\partial P]_T$

16. A gas obeys the relation $P(v-b) = RT$. Show that

$$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{C_v}{R + C_v} \cdot \frac{V-b}{P}$$

17. One mole of Argon initially at 1 atm. and 0°C was heated to a temperature of 150°C. Show that its entropy will remain unchanged if the pressure be also raised to 1.99 atm.

18. The van der Waals constants for air are $a = 13.5 \times 10^5$ atm.-c.c^2 and $b = 36.5$ c.c., and its heat capacity, $C_p = 7.0$ cal/mole. Calculate the inversion temperature.

What will be the drop in temperature if the air at 0°C is allowed to expand by throttling from 200 atmos to 2 atoms.

19. Show that C_V for a van der Waals gas is independent of pressure or volume. Also show that $C_P - C_V$ for such a gas would pass through a maximum as the pressure is increased.

20. If the Gibbs' function includes magnetic properties, then it may be represented as $G = U - TS - \mathscr{H}\mathscr{I}$

Show that (i) $\left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \left(\frac{\partial \mathscr{I}}{\partial T}\right)_{\mathscr{H}}$

$$\text{(ii)}\ \left(\frac{\partial T}{\partial \mathscr{H}}\right)_S = -\mathscr{H}T\left(\frac{\partial X}{\partial T}\right)_{\mathscr{H}} \Big/ C_{\mathscr{H}}$$

where X is the molar susceptibility.

21. Show that

$$\ln\frac{P}{P_0} = \frac{2\sigma}{r\rho} \cdot \frac{M}{RT}$$

When P = Vapour pressure of a drop of liquid of radius r

P_0 = Vapour pressure over a mass of the same

σ = Surface tension of the liquid

ρ = Density of the liquid

22. The heat of vaporization of cyclohexane (b. pt. 80°C) is 85 calories/gm. The specific densities of the liquid and the vapour at this temperature are 0.72 and 0.003 gm. Find out the pressure at which the liquid can be distilled at 30°C.

23. Show that the increase of pressure would raise the freezing pt. of a liquid which contracts on freezing.

24. The heat of fusion of ice at 0°C is 1440 cal per mole. The change in specific volume on melting is -0.09 c.c. per gm.

(*a*) Calculate the slope of the fusion curve of ice at the normal melting point.

(*b*) Ice at -5°C is compressed isothermally. At what pressure would it start to melt.

(*c*) Ice at -5°C and atmospheric pressure is kept enclosed at constant volume, and the temperature is gradually increased. Find the temperature and pressure at which the ice starts to melt.

25. It is an empirical rule that the boiling point (T_b) of a substance is two-thirds of its critical temperature (T_c). For methanol, $T_c = 513$°K. Estimate its heat of vaporisation. **Ans.** 71800 cal/mole

26. Show that the relative variation of the boiling temperature is one-tenth the relative variation of pressure, provided the vapour behaves ideally and obey's Trouton's law.

27. Show that in saturated solutions the concentration is related to the pressure applied to the system by the equation,

$$\left(\frac{\partial \log C_s}{\partial P}\right)_T = -\frac{\Delta V}{RT}$$

where ΔV is the incerase in volume of the solution on dissolving one mole of solute.

28. At the λ-pont (2.19°K) the two forms of liquid He I and He II have the following heat-capacities and volume coefficients

$C_{P_I} = 1.2$ cal/gm $\qquad \alpha_I = 0.02$ per degree

$C_{P_{II}} = 2.85$ cal/gm $\qquad \alpha_{II} = -0.039$ per degree

and the volume is 6.84 c.c./gm. Calculate the variation of the λ-point pressure with temperature.

Hint. $$\frac{dP}{dT} = \frac{C_{P_I} - C_{P_{II}}}{TV(\alpha_I - \alpha_{II})}$$

29. Prove that the slope of the sublimation curve at the triple point is greater than that of the vaporisation curve at the same point.

30. According to Debye, the molar heat-capacity of a solid at low temperatures is expressed as $C_p = aT^3$. For a given solid, it was found that C_p at 10°K is 0.797 cal/degree. Show that the molar entropy of the solid at 10°K is 0.266 e.u.

31. The m.pt. of salol is 42°C and that of diphenyl is 70°C. The eutectic composition is 27% diphenyl by weight at temperature, 24°C. Calculate the molar heats of fusion of the two components, assuming ideal behaviour. (mol. wt. of Salol = 214, mol wt. of diphenyl = 154).

32. At 25°C, the e.m.f. of the cell :

$$\text{Zn}-\text{ZnCl}_2 \text{ (soln)} \parallel \text{Hg}_2\text{Cl}_2-\text{Hg}$$

is 1.027 volts and the temperature coefficient of the e.m.f. is 1×10^{-4} volt per degree. Calculate the heat of reaction.

33. Find out the free energy change and also the heat of reaction of the chemical process occurring in the weston cell at 25°C.

$$Hg-Hg_2SO_4 \parallel CdSO_4 \text{ (sat.)} \parallel CdSO_4,\ 8/3H_2O^{-}(Cd)_x\text{-}Hg.$$

The e.m.f. of the cell at t°C is given by :

$$E_t = 1.0186-3.8\times10^{-5}(t-20)$$

34. Find the activity product of silver chloride in saturated solutions, using the standard electrode potentials of the Ag/Ag^+ and $Ag/AgCl-Cl^-$ electrodes.

35. The K_a for acetic acid is 1.808×10^{-5}. Calculate the degree of dissociation of 0.02 molar acid in 0.02 sodium chloride. (Use Debye-Hückel law and neglect H^+ ion concentration)

36. In a parchment bag, 10 gm of a colloidal acid (HR) dissolved in a litre of dilute HCl was taken and kept suspended in a litre of pure water at 25°C. At eqm. the pH of the external water was found to be 3.6 and the membrane potential 0.036 volts. What is the pH of the solution inside the bag? Calculate also the molecular weight of the colloidal acid.

[*Note* : Let initial conc. of colloid acid and HCl be a and b moles/litre.

At eqm. outside : $c_{H^+} = c,\ c_{Cl^-} = c$

and inside : $c_{H^+} = a+b-c, \quad c_{Cl^-} = b-c, \quad c_{R^-} = a$

Further $(a+b-c)\,(b-c) = c^2$,

since $\quad c_{H^+(in)}.c_{Cl^-(in)} = c_{H^+(out)}.c_{Cl^-(out)}$

Given $\quad \log_{10}\dfrac{1}{c} = 3.6, \quad c = 2.5\times10^{-4}$

also $e_{mem} = 0.059 \log \dfrac{c_{H^+(in)}}{c_{H^+(out)}} = 0.059\ [pH_{out} - pH_{in}]$ volts.

Calculate $pH_{(in)}$. Next solve for $(b-c)$, since

$2 \log c = \log (b-c)+\log (a+b-c)$, remember $\log (a+b-c) = -pH_{(in)}$.]

37. Starting with equation, $E = \sum\limits_{0}^{\alpha} n_i\varepsilon_i$,

Show that the thermal energy of an ensemble of one-dimensional harmonic oscillator is $Nh\nu\ [e^{h\nu/kT}-1]^{-1}$

38. The vibrational frequency of a diatomic gas is 667.3 cm^{-1}. What percentage of molecules are in their first excited state at 27°C? [Ans. 3.9%]

39. 36.8% $\left(=\dfrac{1}{e}\right)$ of the diatomic gas of problem 38 ($\nu = 667.3\ cm^{-1}$) are present at the first excited state. What is the temperature of the gas?

[Ans. T = 958°K]

40. The statistical entropy of a monatomic ideal gas,

$$S = \tfrac{5}{2}R\ln T - R\ln P + \tfrac{3}{2}R\ln M + \mathrm{K}$$

Evaluate K and hence compute the standard entropy of Neon.

41. The thermal decomposition of NOCl is

$$2\mathrm{NOCl} \rightarrow 2\mathrm{NO} + \mathrm{Cl_2}\ ;\ \Delta H^\circ = +77.07 \text{ kj}$$

The molar entropies are

$$S_{\mathrm{NOCl}} = 261.6,\ S_{\mathrm{NO}} = 210.7,\ S_{\mathrm{Cl_2}} = 223.0 \text{ joules/°K.}$$

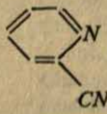
ΔH and ΔS are supposed to be temperature invariant.

Calculate the eqm constant for the reaction at 650°K.

[Ans. K $=1.36$; $\Delta G = -1.66$kj]

42. The heat of combustion of isoprene (C_5H_8) is -746 kcal/mole. Calculate its heat of formation. By using bond energy calculatoins, estimate the resonance energy of isoprene.

43. A synthesis of cyanopyridine is attempted as

$C_4H_6(g) + C_2N_2(g) \rightarrow$  $+ H_2$

Butadiene cyanogen α-cyanopyridine

Is the synthesis possible ? Given molar values at 298°K

	Butadiene	Cyanogen	Cyanopyridine	hydrogen
ΔH_f° (kcal)	26.8	71.8	62.0	0
ΔS° (cal/°K)	66.4	57.6	77.0	31.2

44. Prove that the slope of the sublimation curve at the triple point is greater than that of the vaporisation curve at the same point.

Estimate the heat of sublimation of ice at −20°C from the following vapour pressure data :

t°C	-19.5°	-20°	-20.5°
p(mm)$\times 10^2$	80.8	77.0	73.4

[Ans. $l_s = 28\times10^5$ j/kg]

45. In a diesel engine the air-oil vapour mixture ($\gamma = 1.3$) is taken in at 1 atm and 15°C. It is compressed rapidly to 1/15th of its orgnial volume. What are the temperature and pressure when the compression is complete?

[Ans. p = 33.8 atm, t = 377°C]

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